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CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

General, Physical, and Inorganic.

PAGE

94. Factors Influencing the Strengths of Bonds.
By A. D. WALSH 398

95. Excited States of Benzene. Part I. Introductory Consideration of Some Spectral Properties of Vibrations accompanying Electronic Transitions of Benzene and Deuterated Benzenes.
By FRANCESCA M. GARFORTH, CHRISTOPHER K. INGOLD, and HARRY G. POOLE . 406

96. Excited States of Benzene. Part II. Analysis of the First Ultraviolet Band System of the Absorption Spectrum of Benzene.
By FRANCESCA M. GARFORTH and CHRISTOPHER K. INGOLD 417

97. Excited States of Benzene. Part III. Analysis of the First Ultraviolet Band System of the Fluorescence Spectrum of Benzene.
By FRANCESCA M. GARFORTH and CHRISTOPHER K. INGOLD 427

98. Excited States of Benzene. Part IV. Analysis of the First Ultraviolet Band System of the Absorption Spectrum of Hexadeuterobenzene.
By FRANCESCA M. GARFORTH and CHRISTOPHER K. INGOLD 433

99. Excited States of Benzene. Part V. Analysis of the First Ultraviolet Band System of the Fluorescence Spectrum of Hexadeuterobenzene.
By FRANCESCA M. GARFORTH and CHRISTOPHER K. INGOLD 440

100. Excited States of Benzene. Part VI. Description and Analysis of the First Ultraviolet Band System of the Absorption Spectrum of 1 : 3 : 5-Trideuterobenzene.
By FRANCESCA M. GARFORTH, CHRISTOPHER K. INGOLD, and HARRY G. POOLE . 445

101. Excited States of Benzene. Part VII. Description and Analysis of the First Ultraviolet Band System of the Fluorescence Spectrum of 1 : 3 : 5-Trideuterobenzene.
By ARTHUR P. BEST, CHRISTOPHER K. INGOLD, and CHRISTOPHER L. WILSON . 456

102. Excited States of Benzene. Part VIII. Description and Analysis of the First Ultraviolet Band System of the Absorption Spectrum of 1 : 4-Dideuterobenzene.
By FRANCESCA M. GARFORTH, CHRISTOPHER K. INGOLD, and HARRY G. POOLE . 461

103. Excited States of Benzene. Part IX. Description and Analysis of the First Ultraviolet Band System of the Absorption Spectrum of 1 : 2 : 4 : 5-Tetradeuterobenzene.
By FRANCESCA M. GARFORTH, CHRISTOPHER K. INGOLD, and HARRY G. POOLE . 475

104. Excited States of Benzene. Part X. Analysis of the First Ultraviolet Band System of the Absorption Spectrum of Monodeuterobenzene.
By FRANCESCA M. GARFORTH and CHRISTOPHER K. INGOLD 483

105. Excited States of Benzene. Part XI. Comparisons between the First Ultraviolet Absorption and Fluorescence Band Systems of Isotopically Isomeric Benzenes, and Further Determinations of the Vibration Frequencies of the Upper Electronic State.
By FRANCESCA M. GARFORTH, CHRISTOPHER K. INGOLD, and HARRY G. POOLE . 491

106. Excited States of Benzene. Part XII. The Effect of an Electronic Excitation on the Geometry, Elastic Properties, and Zero-point Energy of the Benzene Molecule: and the Effect of Isotopic Substitution on the Transition Energy.
By FRANCESCA M. GARFORTH, CHRISTOPHER K. INGOLD, and HARRY G. POOLE . 508

Organic.

107. Synthesis of Alloxazine from 2-Aminoquinoxaline-3-carboxyamide.
By A. H. GOWENLOCK, G. T. NEWBOLD, and F. S. SPRING 517

108. The Oxidation of 2-Hydroxyquinoxaline and its Derivatives with Hydrogen Peroxide.
By G. T. NEWBOLD and F. S. SPRING 519

PAGE

109. Application of the Hofmann Reaction to the Synthesis of Heterocyclic Compounds. Part V. The Synthesis of 9-D-Mannopyranosidoxanthine and of 9-D-Ribopyranosidoxanthine.
By R. A. BAXTER, A. C. MCLEAN, and F. S. SPRING 523

110. The Synthesis of Some Aryl 2-Thienyl Sulphones and the Nitration of Thiophen-2-sulphonyl Chloride.
By H. BURTON and W. A. DAVY 525

111. The Use of Phenylmagnesium Bromide for the Preparation of Phenyl Aryl Sulphides, Sulphoxides, and Sulphones.
By H. BURTON and W. A. DAVY 528

NOTE—The Action of Hydrogen Chloride on Isoprene.
By A. J. ULTÉE 530

PRESIDENTIAL ADDRESS. Some Aspects of the Chemistry of Hydrocarbons.
By C. N. HINSHELWOOD, M.A., Sc.D., D.Sc., F.R.S. 531

ONE HUNDRED AND SEVENTH ANNUAL GENERAL MEETING 539

INDEX OF AUTHORS' NAMES.

BAXTER, R. A., McLean, A. C., and Spring, F. S., 523.
Best, A. P., Ingold, C. K., and Wilson, C. L., 456.
Burton, H., and Davy, W. A., 525, 528.
Davy, W. A. See Burton, H.
Garforth, F. M., and Ingold, C. K., 417, 427, 433, 440, 483.
Garforth, F. M., Ingold, C. K., and Poole, H. G., 406, 445, 461, 475, 491, 508.
Gowenlock, A. H., Newbold, G. T., and Spring, F. S., 517.
Hinshelwood, C. N., 531.
Ingold, C. K. See Best, A. P., and Garforth, F. M.
McLean, A. C. See Baxter, R. A.
Newbold, G. T., and Spring, F. S., 519.
Newbold, G. T. See also Gowenlock, A. H.
Poole, H. G. See Garforth, F. M.
Spring, F. S. See Baxter, R. A., Gowenlock, A. H., and Newbold, G. T.
Ultée, A. J., 530.
Walsh, A. D., 398.
Wilson, C. L. See Best, A. P.

ERRATA.

VOL., 1947.

Page	Line	
516	4 *	*for* " $C_{13}H_{19}O_9N_4$ " *read* " $C_{13}H_{22}O_9N_4$ ".
517	28 *	*for* " $C_{17}H_{14}O_3NCl$ " *read* " $C_7H_{14}O_2NCl$ ".
1108	6 *	*for* " C, 15·7 " (in two places) *read* " S, 15·7 ".
1115		In table, *for* " Benzylamine " *read* " *cyclo*Hexylamine ".
1116	13 *	*for* " methano " *read* " methanol ".
1458, 1459		Interchange Figs. 1 and 2.
1682	4	*for* " $0{\cdot}00722f^2$ " *read* " $0{\cdot}000722f^2$ ".

VOL., 1948.

220	6 *	*for* " 2 : 4 : 5-triaminopyrimidine " *read* " 2 : 4 : 5-triamino-6-hydroxypyrimidine ".
223	14 *	" " " " " " " "

* From bottom.

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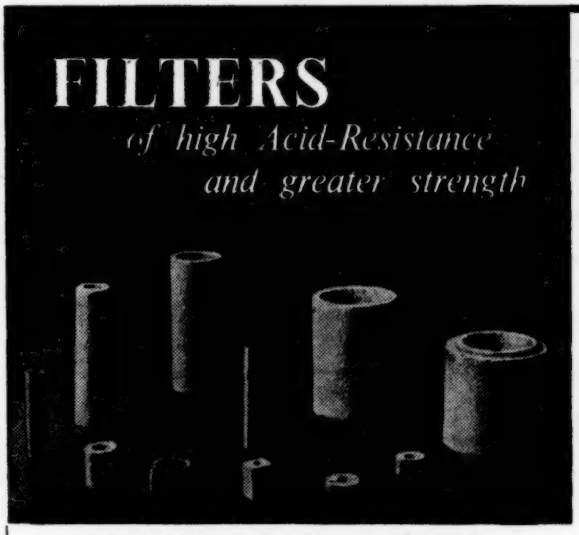

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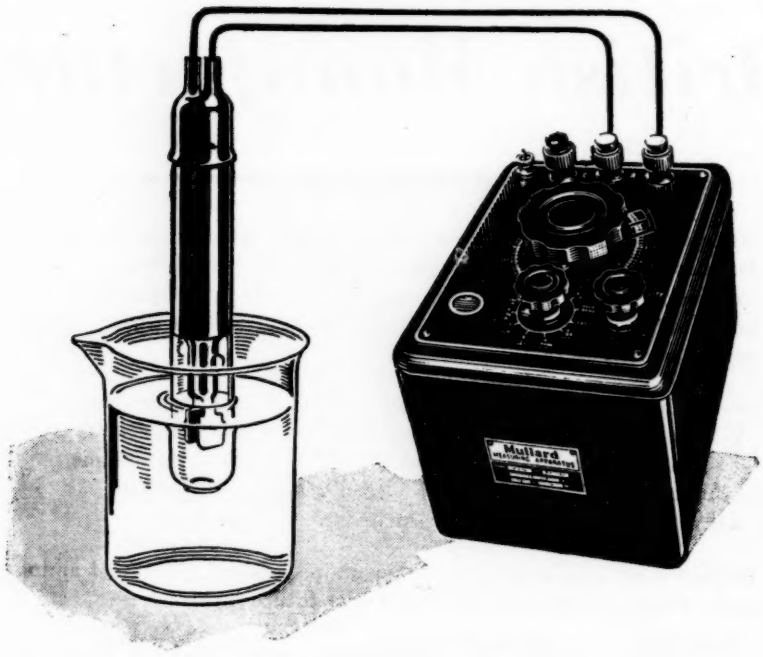

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course of his career, he travelled extensively through India and the Americas on various official and commercial investigations and inquiries.

Lefebure became a Fellow of the Chemical Society in 1913, and an Associate of the Royal Institute of Chemistry in 1918.

He married in 1917 Mary Isabel Clark, of Doncaster, who survives him; he also leaves a son and two daughters.

By the death of Victor Lefebure, the building industry and in particular the Building Industries National Council has lost a distinguished member who has made many noteworthy contributions to its progress and development. His work on cements and plasters had tremendous practical effect on the range and scope of adapted building materials. As Chairman of the Research Committee of the B.I.N.C. he did work which will long be remembered. He also rendered his country good service as a member of various Building and Fire Advisory Committees of the Ministry of Home Security during the last war.

The following extract from an obituary notice by Mr. H. B. Bryant in " The Builder " indicates the high respect in which he was held in the building industries :

> " His painstaking efforts on behalf of practical research into the work of the materials and problems of the building industry will long be remembered with gratitude and with much inspiration by his colleagues. His approach to this side of his interests was marked by a democracy of procedure more than usually rare in this field of activity. In all his dealings in life he was essentially the intelligent but humble democrat. Bureaucracy was to him the cancer of social life. It was because of this quality that he was able to make such a distinguished contribution to both the work and deliberations of B.I.N.C. throughout his association with that body. He was intensely interested in the objects of the Council, as he was in all the many efforts for scientific progress."

Great as were his achievements in the building industry, Victor Lefebure has perhaps a greater international reputation because of his two books, the first " The Riddle of the Rhine " published in 1920, and the second " Scientific Disarmament " published in 1931.

In the " Riddle of the Rhine ", he traced the history of chemical warfare as developed by the Germans in the First World War, and showed the predominant and vital part played by the German Chemical Industry in it. He brought out clearly the great war potentialities of a strong chemical industry and the dangers to future world peace if the German industry was not controlled in some way. His warnings went unheeded, and his prognostications have been completely justified by what took place in the Second World War. Even now the authorities appear to have failed completely to appreciate the intrinsic war potential of a powerful chemical industry not only because of the adaptability of its plant and equipment to war-like purposes but what is even more important because of the large cadre of scientists and technicians which it maintains, capable of developing and producing whatever materials may be required for war-like purposes. The treatment which is now being given to the German chemical industry looks like repeating the mistakes made after 1918.

" Scientific Disarmament ", which was prefaced by many distinguished personalities of the day, caused great international interest at the time of the Disarmament Conference in 1932. His main objective was to stimulate and obtain a real international effort to limit the unleashed forces of national armament development which in his opinion could lead only to war. He reproached scientific men for the readiness with which they gave their knowledge and inventive ability to the needs of national armament. He wanted a new scientific morale in regard to war—a cosmopolitan or international morale. The book was written on idealistic lines, and, while it contained many valuable suggestions which merited more study than they received, it failed to appreciate adequately the problem of bad faith and the impossibility, where bad faith existed, of devising any international machinery which could effectively carry out the objects in view. Nevertheless, the book will well repay detailed study at the present time in connection with the problems of future world peace.

As a man of science, Lefebure added to a high degree of professional competence a stimulating originality of outlook, the ability to present his ideas in a reasoned and interesting manner, and the drive and energy to carry his technical achievements through to the stage of exploitation—gifts which are given to but few.

As a man, he was an outstanding though modest personality with a very lovable character. In spite of the fact that he was a crusader and an iconoclast he was a true and loyal friend. His passing is an intense personal loss to his colleagues in the Building Industries.

J. Davidson Pratt.

ALFRED WALTER STEWART.

1880—1947.

ALFRED WALTER STEWART was born at Glasgow in September, 1880. He was the youngest of three sons of the Rev. Dr. Stewart, Clerk to the University Senate and Professor of Divinity. There is no doubt that Stewart inherited many mental gifts from his father, and he found that the library in his home provided an abundant source of information on many attractive subjects. Thus at an early age his inborn appetite for literature was stimulated. After attending Glasgow High School he entered the University, and in 1907 he graduated, taking chemistry as his chief subject; his outstanding performance in this examination earned him the Mackay-Smith scholarship. Stewart spent another year at Glasgow University during which he found time to make fuller use of the University library and thereby laid the foundation of the extensive knowledge and literary capacity which was characteristic of his later life.

After spending the succeeding year at Marburg, where he was engaged in research under Professor Zincke, he was elected to an 1851 Exhibition Scholarship and then (1903) entered University College, London. Here he began his first independent research. This dealt with the activity of aliphatic ketones in their reaction with bisulphite and hydroxylamine. It was found (1905) that substitution by alkyl at the α-carbon atom diminished the rates of oximation and bisulphite addition. This fact appeared to be well explained by the theory of steric hindrance which was prevalent at the time; but when Stewart found that other groups, notably carbethoxyl, produced the reverse effect, he concluded that current theory was inadequate and needed revision. This work, embodied in a Thesis, gained him the D.Sc. degree of Glasgow University, and he was soon elected to a Carnegie Research Fellowship (1905—1908). In the meantime Baly had begun his studies of the selective absorption spectra of organic compounds and had obtained (1905) interesting results from acetoacetic ester and related substances. Stewart now joined forces with Baly, hoping to get further information on his problem. The carbonyl group of ethyl pyruvate had shown remarkable activity, and this ketone was the first subject of their experiments (1906) which were soon extended to α-diketones and to *p*-benzoquinones. It is not possible here to record in detail the interesting results of this collaboration, but it may be said that the chief outcome was the conception that a state of balance existed in the valency distribution of the forms which these substances could assume without shift of any atom. This condition was termed " isorropesis ". To the writer it appears noteworthy that this conception, expressed some twenty years before electronic theory had been extensively applied to organic chemistry, evidently contains a tentative step towards a theory of mesomerism.

At that time little was known of the relations between general absorption and constitution. Stewart now began (1907) a study of these by an examination of fatty acids; he showed that unsaturated acids have a greater general absorption than saturated, and noted that this relation has a parallel in the molecular rotation of their amyl esters. The *trans*-forms of unsaturated acids were found to have greater absorption than the *cis*-forms. Other topics occupied his attention at the same time. He developed a rapid method for determining (1908) the dielectric constants of organic substances with the intention of studying them more fully. Also he began with Wilsmore to examine the pyrolysis of organic compounds by means of a heated platinum wire; these experiments had led (1907) to the preliminary isolation of a substance regarded as keten, but Stewart felt obliged to give up his share of the work owing to pressure of other matters.

He had now decided on an academic career, and being interested in teaching he wrote (1908) " Recent Advances in Organic Chemistry " which was intended to bridge the gap in an advanced student's reading between the usual formal textbook and the *Annual Reports* or original literature. The book proved as welcome to students as Lachmann's " Spirit of Organic Chemistry " had been to those of a former generation, and its success encouraged him to write (1909) a companion volume on Inorganic and Physical Chemistry.

After the Royal University of Ireland had been dissolved, the college at Belfast became the Queen's University, and in the reorganisation which followed Stewart was appointed (1909) to the new lectureship in organic chemistry there. After reorganising the teaching of the subject and providing the equipment which available funds permitted, he resumed his experiments on general absorption. The results of a series of papers (1911, 1912, 1917) may be summed up by the conclusion that conjugation of unsaturated centres leads to the extension of general absorption; the application of this to determining the structure of terpenes was recommended. He also devised (1913) a colour test with tetranitromethane for compounds containing elements capable of undergoing a change of valency. In 1914 he was appointed Lecturer in Physical

Chemistry and Radioactivity in the University of Glasgow, and it is a tribute to his versatility and wide knowledge that he was able to turn with confidence to this post from one in organic chemistry. During the period of the war which followed, much of his time was taken up by work for the Admiralty, and he was unable to resume his own research. It is, however, worth noting that in 1918 he drew attention to the result of a β-ray change in a radio-element and suggested the use of the term " isobar " as complementary to " isotope ".

At the conclusion of the war Professor Letts retired from the Chair of Chemistry at Queen's University, and Stewart was elected (1919) to succeed him. Returning to Belfast, Stewart found an arduous task before him. The difficulties of accommodation which most Universities suffered at that time were increased by his desire to extend the advanced teaching of the subject and particularly by the need of providing and equipping a new laboratory for physical chemistry. With the funds available the last object could not be quickly attained, but after a few years of patient economy he was able to take up research again. His interest had been attracted by some experiments of Wiedemann, who had obtained (1895) continuous emission spectra from a few organic substances by submitting their vapour to the discharge of an induction coil. The method was confined to the more stable hydrocarbons, the majority of carbon compounds being merely decomposed. Stewart and his colleagues found (1923, 1924, 1929) that by using the discharge of a high tension transformer and by reducing the vapour pressure of the substance examined it is possible to obtain pure emission spectra from substances of even moderate stability. Examination of a large number of substances showed relations between the chemical nature of a compound and the type of luminescence which it emits. Certain general types of structure were found to be associated with emission in definite parts of the spectrum. Five chief regions of this kind can be detected, and if a substance contains more than one luminescent group the emission may be extended to more than one region. The effect of simple substituents on the fundamental group could also be traced; some, such as amino- or hydroxyl, shift the luminescence to the red end of the spectrum, and others towards the violet. It is remarkable that the carbonyl group and the benzene nucleus are the only simple systems capable of emitting luminescence, and of these the latter is the more interesting. The seventy fine bands of the benzene luminescence spectrum can be resolved into eight groups each of which in its internal structure resembles its neighbours. Moreover the bands of each group fall into five series in which the arrangement clearly indicates the super-position of five rotation-spectra on one another. After discussing the possible modes of vibration of the benzene ring, Stewart was able to explain the influence of substitution by simple groups on the luminescence. Another interesting feature of this emission spectrum of benzene lies in the fact that it was found to be the reversal of the absorption spectrum; this was the first instance of the Frauenhofer effect observed in a complex molecule.

Much of Stewart's time during his early years at Belfast was taken up by reorganising the teaching; all branches of the work interested him. He was an attractive lecturer. His first year course was illuminated by his sense of humour and wide culture, and his lectures were illustrated by numerous experiments which were continually being improved; some of his inventions were published (1912). His work as a teacher is reflected by the success of his advanced students. He endowed them with something of his own critical powers and independent thought. The fact that so many of them occupy responsible positions in nearly all branches of the profession shows the quality and breadth of their training.

Stewart was not a man of great physical energy, but any lack of this quality was more than balanced by his extraordinary mental activity. It was his custom on returning home from a day's work at the University to spend the evening or sometimes, indeed, most of the night, in discussions with any friends who might have called on him, or in literary work. He enjoyed writing on any subject and found relaxation in it, in fact it became his hobby. At first this interest was satisfied by writing his scientific publications and succeeding editions of his textbooks, but to anyone who knew Stewart and his store of literary knowledge it was not at all surprising when he published his first novel (1923). This was " Nordenholt's Million " which perhaps is the most remarkable of all those he wrote; recently (1947) it has attained a wide circulation in a popular form. Soon afterwards it was followed by " Almighty Gold ", in which he astonished and amused his friends by a profound knowledge of dubious methods of finance. These and all the novels he subsequently wrote were published under the name " J. J. Connington "—the surname being adopted with slight modification from the translator of Horace. For some years he had suffered from deafness; he now found that it was increasing, and felt obliged to face the prospect that in the not far distant future he might be unable to continue an academic career. Accordingly he decided to pursue his literary work, and turned to detective fiction. In

his spare time during the years which followed he wrote seventeen novels of this character, nearly all of them being composed in the hours around midnight. In these he made full use of scientific methods and facts which were presented with an accuracy and clarity unusual in this type of novel. Some were translated into four or five other languages; in fact, their success ultimately gained him an international reputation. Stewart was of course gratified by this result of so much labour, but he found even greater pleasure in the literary friendships which ensued. His correspondence became extensive, and his help to other authors was freely and happily given. His last book was published shortly after his death; it appeared under his own name and bore the title " Alias J. J. Connington ". Although not an autobiography, this book provides more information of Stewart himself and his wide interests than the writer can hope to have given in this notice.

While Stewart was thus engaged in the twofold task of academic and literary work he found that his sight was failing; the cause was later found to be cataract, and was soon remedied by operation. Apart from a keen interest in the possible causes of the condition and some regret concerning the interruption of his work, Stewart seemed to treat the matter lightly. A few months later symptoms of heart trouble appeared; these increased until in 1944 he felt obliged to resign from his chair at the University; soon afterwards the title of Emeritus Professor was conferred on him. Although now in failing health he continued his literary work as usual until he passed away while engaged with it in the early morning of July 1st, 1947.

Stewart was a man of calm and resolute courage. In spite of the afflictions and physical distress he was called upon to endure his sense of humour and his vivid interest in life and humanity remained undimmed; never at any time, even to those most intimate with him, did he utter complaint. He preferred to treat his constant and increasing burden as a matter for philosophic discussion and psychological study. By his death the profession of chemistry has lost a talented scholar and one whose wide culture enabled him to view the science against the larger background of human endeavour. There are some, too, not all of them chemists, who mourn the loss of a true and kindhearted friend.

In 1916 Stewart married Miss Lily Coats, daughter of the Rev. Jervis Coats of Glasgow; she and a daughter survive him.

S. Smiles.

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94. *Factors Influencing the Strengths of Bonds.*

By A. D. Walsh.

An attempt is made to analyse, for use particularly by chemists, some of the factors influencing the strengths of bonds. The discussion is in qualitative terms under the heads : electronegativity of bonded groups, bond polarity, overlap of atomic orbitals, repulsion of filled atomic orbitals, stability of fission fragments.

There can be few questions of greater importance of chemistry than that of " What factors influence the strengths of bonds? " There are numerous such factors and no theory which tries to explain bond-strength variations in terms of one factor alone can be entertained. We shall here be concerned with factors that the chemist—as distinct from the mathematical physicist—can grasp and apply to the particular molecules in which he is interested. We shall discuss various relevant factors under the five headings noted above, but do not claim that the explanation of varying bond strengths could not be analysed into other and more numerous factors. Nevertheless, we believe these five factors to be of prime utility to chemists.

Distinction between Bond and Dissociation Energies.—It is important to draw a distinction between bond energy and dissociation energy (cf. Skinner, *Trans. Faraday Soc.*, 1945, **41**, 645; Long and Norrish, *Proc. Roy. Soc.*, 1946, ***A***, **187**, 337). By bond energy (E) we mean an energy quantity which is a simple measure of the strength of the bond *as it exists in the molecule*. The dissociation energy (D), on the other hand, is the difference of energy between *two* systems, *viz.*, the molecule in its equilibrium configuration and the two portions after fission of the bond under consideration. Clearly, we have no right to expect D to bear a smooth relation to (say) the equilibrium internuclear distance (r) of the bond or to the force constant (k) characterising the curvature of the equilibrium minimum on the potential energy surface. In contrast, E *should* bear such relation. How values are assigned to E is discussed below.

In a diatomic molecule, E is usually equal to D. In some cases, however, the molecule must be regarded as " built " from excited rather than ground-state atoms, so that E is greater than D (Long and Norrish, *loc. cit.*). For example, there are reasons for regarding the oxygen

molecule as partly built from excited atoms (see Walsh, this vol., p. 331). In general, however, the bond energy of a diatomic molecule is approximately equal to the dissociation energy. The word "approximately" is used because the act of dissociation must slightly affect the non-bonding electrons in the molecule, so that D is not quite equal to the "true" E characteristic of the molecule in its equilibrium state: H_2 with no non-bonding electrons is an obvious exception here. In general, the difference between D and E arising from this cause will be small and we shall neglect it: it will, however, limit the precision with which E can be defined.

For polyatomic molecules, the dissociation energy of a bond may frequently differ considerably from the bond energy. This is because the strengths of the remaining bonds in the molecule alter at the moment of fission. As an example, the OH bond is known (from length and force-constant data) to be appreciably stronger in the water molecule than in the OH radical. Consequently, energy must be absorbed by the remaining OH bond when one OH bond in water is broken. Hence $D(\mathrm{H{-}OH})_{H_2O} > E(\mathrm{H{-}OH})_{H_2O} > D(\mathrm{O{-}H})_{OH\ rad.}$. $D(\mathrm{H{-}OH})_{H_2O}$ and $D(\mathrm{O{-}H})_{OH\ rad.}$ are respectively ~118 and ~100 kcals./mole (Dwyer and Oldenberg, *J. Chem. Physics*, 1944, **12**, 351); $E(\mathrm{H{-}OH})_{H_2O}$ is 110 kcals./mole.

For molecules of type XY_n, $E(XY) = Q_a/n$ where Q_a is the heat liberated when the atoms, in their appropriate valence states, combine to form the molecule. Thus for the water molecule, if Q_a is taken as 220 kcals./mole, $E(OH)_{H_2O}$ is 110 kcals./mole. For CH_4, if we consider the valency state of the carbon atom to be 65 kcals. above the ground state (Long and Norrish, *loc. cit.*), then $Q_a = 416$ kcals./mole and $E(CH)_{CH_4} = 104$ kcals./mole. In distinction to dissociation energies, bond energies in polyatomic molecules are not capable of definition with complete precision. The concept presupposes a localised-pair bond theory without interaction between different bonds. In fact, as four hydrogen atoms and one carbon atom are brought together to form CH_4, though most of the energy liberated is due to the overlap of electron clouds in the four resulting CH bonds, a little is due to overlap not in the CH bonds. The wave functions for the bonding electrons in methane (Coulson, *Trans. Faraday Soc.*, 1942, **38**, 433) can be expressed as $\psi_A = t_A + k_1A + k_2(B + C + D)$ where A is one hydrogen atom and B,C,D the others; and where k_2 represents a small non-localisation term, perhaps one-fiftieth of the term $t_A + k_1A$. In the same way, the "force constant" of a bond in a polyatomic molecule is affected by the neighbouring bonds and cannot be considered in *complete* isolation. Thus, too, the ionisation potential (I) of the electrons in a bond does not solely concern that bond—the bonding effect is not confined to it but is spread a little over all the other bonds. However, the smallness of the non-localisation effect in many molecules still makes "bond quantities" very useful. In molecules like methane the approximation involved in speaking of E, k, I, etc., as referring to a particular bond is not serious, though in carbon tetrachloride it may be more important (Cl–Cl interaction being known to be important in this molecule; Walsh, *Trans. Faraday Soc.*, 1947, **43**, 60). The concept of bond energy has at least as much precision as have the bond diagrams that have been so useful to chemists.

For molecules with different types of bond the definition of E is not so clear. In such cases, the bond energies must be so chosen that (*a*) their sum equals Q_a, (*b*) they serve as useful parameters for interconversion of bond properties, standard points for the interconversion relations being provided by XY_n molecules. For example, in hydrogen peroxide, Q_a may be taken as 256 kcals. Comparison of (*a*) the length and (*b*) the force constant of OH bonds in water, the hydroxyl radical, and hydrogen peroxide shows that the bond is slightly weaker in hydrogen peroxide than in the hydroxyl radical, which in turn is weaker than the OH bond in the water molecule. A choice of 96 kcals./mole for $E(OH)_{H_2O_2}$ seems a fair one [that is, a few kcals. less than $E(OH)_{OH\ rad.}$; Walsh, this vol. p. 331]. Consequently, $E(OO)_{H_2O_2}$ must be chosen as ~64 kcals./mole, and this may be shown to be roughly consistent with the known strengths and properties of similar bonds.

In view of the foregoing it is unnecessary to stress that bond energies are not constant from molecule to molecule. We have already mentioned as an example the variation in the OH bond energy from water to OH to hydrogen peroxide.

Electronegativities of Bonded Groups.—Since the binding of electrons in a molecular orbital is related to that in the atomic orbitals from which the molecular orbital has been constructed, one expects bond strength to increase (other things being equal) with increase of electronegactivity of one or both of the bonded atoms. There are abundant examples of the truth of this (cf. Gordy, *J. Chem. Physics*, 1946, **14**, 305). Force-constant and energy data show that $E(\mathrm{H{-}F})_{HF} > E(\mathrm{H{-}OH})_{H_2O} > E(\mathrm{N{-}H})_{NH_3} > E(\mathrm{C{-}H})_{CH\ rad.}$, all these being compounds in which the atom bound to H uses a ground state valency configuration. [$E(\mathrm{H{-}F})_{HF} = 148$ kcals./mole (Skinner, *Trans. Faraday Soc.*, 1945, **41**, 645); $k(\mathrm{H{-}F})_{HF} = 9{\cdot}62 \times 10^5$ dynes/cm. (Linnett, *ibid.*,

1945, **41**, 223); $E(H{-}OH)_{H_2O} = 110$ kcals./mole (Pauling, "Nature of the Chemical Bond," Cornell, 1940); $k(H{-}OH)_{H_2O} = 7{\cdot}66 \times 10^5$ dynes/cm. (Herzberg, "Infra-red and Raman Spectra," Van Nostrand, 1945); $E(N{-}H)_{NH_3} = 93$ kcals./mole, assuming $D(N_2) = 225$ kcals./mole (Skinner, *loc. cit.*); $k(N{-}H)_{NH_3} = 6{\cdot}5 \times 10^5$ dynes/cm. (Linnett, *loc. cit.*); $E(C{-}H)_{CH\ rad.} = 80$ kcals./mole (Herzberg, "Molecular Spectra and Molecular Structure," Prentice Hall, 1939); $k(C{-}H)_{CH\ rad.} = 4{\cdot}09 \times 10^5$ dynes/cm. (Herzberg, 1945, *loc. cit.*).]

Thermochemical and other data show that

$$\underset{64}{E(O{-}O)_{H_2O_2}} > \underset{54}{E(S{-}S)_{S_8}} > \underset{41}{E(Se{-}Se)_{Se_8}} \text{ kcals./mole}$$

(Skinner, *loc. cit.*; Walsh, this vol., p. 331). Similarly,

$$\underset{64}{E(F_2)} > \underset{58}{E(Cl_2)} > \underset{46}{E(Br_2)} > \underset{36}{E(I_2)} \text{ kcals./mole}$$

(Skinner, *loc. cit.*), and, indeed, any bond XX increases in strength as X decreases in atomic weight in any group of the Periodic Table. For example, energy data (Skinner, *loc. cit.*; Walsh, in the press) suggest that

$$\underset{64}{E(N{-}N)_{N_2H_4}} > \underset{44}{E(P{-}P)_{P_4}} > \underset{34}{E(As{-}As)_{As_4}} \text{ kcals./mole}$$

and

$$\underset{95}{E(C{-}C)_{C_2H_6}} > \underset{51}{E(Si{-}Si)_{Si_2H_6}} > \underset{34}{E(Ge{-}Ge)_{Ge_2H_6}} \text{ kcals./mole.}$$

Force-constant data show that

$$\underset{7{\cdot}7}{k(O{-}H)_{H_2O}} > \underset{4{\cdot}1}{k(S{-}H)_{H_2S}} > \underset{3{\cdot}2 \times 10^5}{k(Se{-}H)_{H_2Se}} \text{ dynes/cm.}$$

(Herzberg, 1945, *loc. cit.*).

An important point that should be considered here is the relation of electronegativity to the hybridisation of the 2*s* and 2*p* atomic orbitals. It is possible to show (Coulson, V. Henri Memorial Vol., Desoer, Liége, in the press) that the average value of the position of an electron lies further from the nucleus for the 2*p* than for the 2*s* orbital. We may therefore state that a carbon atom has a greater electronegativity when exerting a 2*s* than when exerting a 2*p* valency. The same applies to a boron or a nitrogen atom and is to be expected from the drop in first ionisation potential as we pass from beryllium to boron: evidently the 2*p* electrons are less strongly bound than are the 2*s*. In a hybrid valency, it therefore follows that the atom concerned has a greater electronegativity the greater the proportion of *s* character in its valency. Table I shows examples of this.

TABLE I.

Molecule.	Hybridisation state of C valencies used in σ bonds.	
CH radical	pure *p*	↓ electronegativity of C atom in bonds increasing.
CH_4	sp^3, tetrahedral	
C_2H_4	sp^2, trigonal	
C_2H_2	*sp*, digonal	

The acidity of acetylene supplies direct confirmation of the present reasoning, as does the finding by Braude and Jones (*J.*, 1946, 128), from studies of reaction velocity (in reactions requiring electron accession at the reaction centre), that an acetylenic carbon atom has a much larger electron-attracting nature than has an ethylenic one. Similarly, propiolic acid ($CH{:}C{\cdot}CO_2H$) has a much higher dissociation constant than has acrylic acid ($CH_2{:}CH{\cdot}CO_2H$). In consequence of the facts embodied in Table I, the CH bond strength should become greater as we descend the table. That this is so is shown by Table II.

TABLE II.

Molecule.	$10^{-5}k$(CH), dynes/cm.	r(CH), A.	E(CH), kcals./mole.
CH radical	4·09	1·120	80
CH_4	4·97	1·094	104
C_2H_4	5·1	1·087	106
C_2H_2	5·85	1·059	121

The greater strength of the vinyl–Cl bond (shorter length and higher force constant) than of the methyl–Cl bond is usually ascribed exclusively to resonance involving the lone-pair Cl electrons. That this is not satisfactory is seen by the fact that vinyl–H is also strengthened relatively to methyl–H, H having no lone-pair electrons. Instead, a large part of the strengthening is due to the change of electronegativity with increasing *s* character in a hybrid valency. *All* vinyl–X bonds are strengthened relatively to methyl–X.

The CC bond in ethane forms another example of bond strengthening due to admixture of 2*s* with 2*p*. The NN bond in hydrazine, the OO bond in hydrogen peroxide, and the FF bond in fluorine all have closely the same strength (Walsh, this vol., p. 331). We might expect the CC bond in ethane to have a strength very similar to these other bonds. In fact, it is considerably stronger, as shown by its force constant and bond energy. Skinner (*Nature*, 1946, **158**, 592) has shown unambiguously that $D(CC)_{C_2H_4} = 84{\cdot}3$ kcals./mole. Now the free methyl radical uses sp^2 carbon valencies and therefore each CH should be much as in C_2H_4, that is, ~2 kcals. stronger than in C_2H_6 or CH_4. Hence $E(CC)_{C_2H_4}$ is certainly greater than 84·3 kcals. and may be as high as 96 kcals.; *D* is low because CH changes in strength from C_2H_6 to CH_3. In view of the very small interaction of CC or CH bonds attached to the same carbon atom, it seems probable that $E(CC)_{C_2H_4}$ is close to $E(CC)_{diamond}$, which is $L_2/2$, where L_2 is the latent heat of sublimation of carbon to the quadrivalent state. Hence if $L_2 \simeq 190$ kcals. (Long and Norrish, *loc. cit.*), $E(CC)_{C_2H_4} \simeq 95$ kcals.

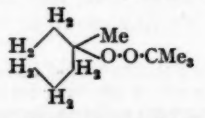
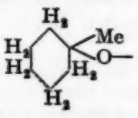
If two of the hydrogen atoms of ethane are changed to give the compound $CH_2X{\cdot}CH_2X$, where X is a group of higher electronegativity than H, then the strength of the central CC bond should be increased; X may be CO_2H as in succinic acid or a phenyl group as in dibenzyl. Since an unsaturated carbon atom has a high electronegativity, X may also be the group C≡C–. In this way, Bateman and Jeffrey's finding (*Nature*, 1943, **152**, 446; Jeffrey, *Proc. Roy. Soc.*, 1945, *A*, **183**, 388) that the central bond of the group C≡C—C—C—C≡C is significantly shorter than the CC bond of ethane causes no surprise. The effective electronegativity of the central C atoms is increased without introduction of polarity (see below). This is a particularly good example of the distinction between *D* and *E*. The allyl radical is so stable (see below) that there is little doubt that the dissociation energy of the central CC bond of the group C≡C—C—C—C≡C would be abnormally low, whereas the bond energy is abnormally high. Dibenzyl provides a similar example (Jeffrey, *Nature*, 1945, **156**, 82; *Proc. Roy. Soc.*, 1947, *A*, **188**, 222). If X has a lower electronegativity than H, then *E*(CC) will be less than in ethane. An example is provided by *n*-butane, where the central bond is known to have a low dissociation energy (Skinner, *Nature*, 1946, **158**, 592) and has also a low bond energy. A similar example is seen in *cyclo*hexane, where also the bonds are between secondary carbon atoms and are known to be weaker than in ethane (Walsh, *Trans. Faraday Soc.*, 1946, **42**, 779).* Strain effects (whatever their interpretation in modern orbital theory) of course probably also affect the *cyclo*hexane bonds. In butadiene, even if overlap of π orbitals did not occur, the central CC bond would still be strengthened relatively to ethane, since it is of sp^2–sp^2 type: it is therefore not satisfactory to calculate theoretically the π bond order in the central bond and then to add the ethane CC bond order to this so as to get the total central CC bond order.

Finally, we may point out that the ionisation potentials of non-bonding electrons in the alkyl chlorides and in hydrogen chloride afford a convenient way of assessing relative electronegativities and show that the electronegativity decreases in the series H > Me > Et > Pr^i > Bu^t.

Gordy (*loc. cit.*) has emphasized the importance of electronegativity in determining bond strengths, and has written bond strength as a function of the product (X_AX_B) of the electronegativities of the bonded groups. That other factors cannot be neglected, however, will be stressed in following sections.

The Polarity of Bonds.—If electronegativity were the only factor affecting the strength

* The decomposition of peroxides supplies much data on relative bond strengths. Peroxides of type R·O·OR break at the O–O bond and then at the weakest bond, other than the C–O, on the α-carbon atom (*idem, ibid.*, p. 269). Thus the peroxide (I) yields the radical (II) and then breaks at a ring C–C

(I).   (II.)

bond in preference to the C–CH_2 bond (Milas and Perry, *J. Amer. Chem. Soc.*, 1946, **68**, 1938). This confirms the weakness of the ring C–C strength. Similarly, in an alkoxy-radical $CR_1R_2R_3{\cdot}O{\cdot}$, the carbon bond to break is that to the alkyl group with the least electronegativity.

of bonds, then on replacing an H in ethane by OH the strength of the CC bond should be increased as a consequence of the increase of electronegativity of one of the carbon atoms. In fact the strength appears, from Bonner's simple, but probably significant, force-constant calculations (*ibid.*, 1937, **5**, 293), to be less in ethyl alcohol. The offsetting factor is to be found in the fact that polarity has been introduced into the CC bond which in ethane was non-polar. Keten affords a similar example : the presence of the oxygen atom and the acetylenic nature of the central carbon atom mean that the C⁼⁼C bond is polar, whereas that of ethylene is non-polar. Accordingly, the C⁼⁼C bond does not appear stronger in keten than in ethylene (see Walsh, *Trans. Faraday Soc.*, 1947, **43**, 60), in spite of the raised electronegativity of one of the carbon atoms. In carbon suboxide *all* the carbon atoms are in the acetylenic state : considering the CC bond adjoining a C⁼⁼O, we therefore have a change relative to keten which (*a*) reduces the CC polarity, and (*b*) increases the electronegativity of one of the bonded atoms. These two factors reinforce each other and this CC bond of carbon suboxide, unlike that of keten, becomes stronger than that of ethylene [$k(CC)_{C_2H_4} = 9{\cdot}6 \times 10^5$ dynes/cm. (Herzberg, 1945, *loc. cit.*); $k(CC)_{C_3O_2} = 12{\cdot}7 \times 10^5$ dynes/cm. (Thompson and Linnett, *J.*, 1937, 1376)].

When methyl ether forms its complex with boron trifluoride, $(CH_3)_2O \rightarrow BF_3$, it is clear that the effective electronegativity of the oxygen atom for the C–O bond electrons must increase. Yet the C–O bonds *weaken* on formation of the complex, as a consequence of the increased $\overset{+}{C}\text{–}\overset{-}{O}$ polarity. The length of the B–F bonds also increases on formation of the complex. This is partly because their initial $\overset{+}{B}\text{–}\overset{-}{F}$ polarity increases and partly because the boron valencies change from trigonal to tetrahedral.

Attachment of a hydroxyl group to the oxygen atom of a second hydroxyl group must increase the effective electronegativity of the oxygen atom of the second group. Yet the indications are that the OH strength in H·O·OH is less and not greater than in the free OH radical.

All these cases are examples where a relation, such as that of Gordy (1946, *loc. cit.*), which relates electronegativity and bond strength without taking into account bond polarity, breaks down.* The breakdown will be likely to occur wherever negative charge is taken out of a bond in such a way as to increase the polarity.

The CH radical utilises a pure *p* carbon valency and has therefore a weaker bond than has CH_4 where the carbon atom utilises hybrid sp^3 valencies. In the same way the NH bond in NH_3 (where nitrogen valencies with probably less *s* character than sp^3 are used) might be expected to be weaker than the NH bond in NH_4^+ (using hybrid sp^3 valencies). However, to expect this is to neglect the importance of the bond polarity which must be much greater in NH_4^+ than in NH_3. Accordingly, it appears that $k(NH)_{NH_4^+}$ is less than $k(NH)_{NH_3}$ (Gordy, *loc. cit.*). Further, the NH strength in NH_4^+ might be expected to be greater than the CH strength in CH_4, since N^+ lies at the end of the series Pb, Sn, Si, C, N^+. Yet if $k(NH)_{NH_4^+} < k(NH)_{NH_3}$, $E(NH)_{NH_4^+}$ must be less than 93 kcals., whereas $E(CH)_{CH_4}$ is ~104 kcals. Again, the explanation must be that the vast increase in bond polarity from CH_4 to NH_4^+ more than offsets the increase of bond strength due to increase in electronegativity product. Gordy has implicitly adopted much the same explanation of the weakness of NH in NH_4^+ by describing the bond polarity in terms of resonance structures and considering the resulting " bond order ".

H_3O^+ presumably uses oxygen valencies of much the same hybridisation type as in H_2O. In this case, therefore, there are no opposing factors and the OH strength should be considerably less in H_3O^+ than in H_2O as a result of the greater bond polarity. The infra-red absorption data appear to accord with this (Gordy, *loc. cit.*). In all cases where H_2O is co-ordinated to, say, a metal ion, the strength of the OH bonds should be decreased [cf. the C–O bonds in the complex $(CH_3)_2O \longrightarrow BF_3$].

In former papers we have given much evidence to justify the statement that bond strength decreases with increasing bond polarity. It is of interest to note that the L.C.A.O. approximation of the molecular orbital theory predicts a result in accord with the facts—namely, that bond strength for a given bond decreases with polarity (Coulson, *Proc. Roy. Soc.*, 1939, *A*, **169**, 413). For a single bond between two nuclei A and B, the bonding electrons lie in an orbital of form

* At first sight Gordy's relation suggests that change of polarity would have little effect : it increases X_A but reduces X_B. It is true that Gordy considers a factor *N* allowing for change in " bond order ". One way of making his relation include the bond weakening with polarity increase is to say that increase of polarity causes a decrease in *N* because the charge cloud now extends more and more *outside* the bond; but Gordy himself did not explicitly consider the relation of *N* to polarity increase or to atomic orbital overlap (see below).

$(a\psi_A + b\psi_B)/\sqrt{a^2 + b^2}$. The bond order per electron is then given by the product of the coefficients of ψ_A and ψ_B, *i.e.*, by $ab/(a^2 + b^2)$. This is easily shown to have a maximum value when $a = b$; that is, the binding is a maximum when it is non-polar, but decreases with increasing polarity. (Strictly, the "overlap integral" should be included in the denominator of the expressions for the orbital and the bond order; but its inclusion still leaves the maximum at $a = b$.)

The simple molecular orbital theory thus shows that bonds weaken with increasing polarity. In part, this is because increasing polarity means that the orbitals of the bonding electrons come to extend more and more on the side of one of the atoms away from the bond, where they are lost for bonding purposes and where their screening effect on the repulsion between the nuclei is lost. Nevertheless, this is not the only effect at work. The molecular orbital calculation shows an effect that is too low because it neglects interaction of the bonding electrons with lone-pair electrons on one of the atoms or with electrons in neighbouring bonds. As the polarity of the bond electrons in >C⁼⁼O or ⩾C—Cl increases, we know that the lone-pair electrons on the oxygen or the chlorine atom suffer more and more repulsion. The bond electrons must suffer an equal repulsion. Hence the bond electrons become more weakly bound the greater the polarity. Hence, by the linkage of bond order and ionisation potential (Walsh, *Trans. Faraday Soc.*, 1946, **42**, 779), the bond weakens to an extent over and above that which would occur in the case of H_2 where no lone pair or neighbouring bond electrons are present. Change of polarity will cause least change of bond strength when (*a*) the nuclear charges are low and (*b*) there are no lone-pair electrons on the more negative atom: CH bonds in quadrivalent carbon compounds fulfil these conditions.

The carbonyl molecules form a particularly excellent series in which the gradation of properties can be correlated with change of carbonyl bond polarity (Walsh, *Trans. Faraday Soc.*, 1947, **43**, 158; *J. Amer. Chem. Soc.*, 1946, **68**, 2408). It would be equivalent in this series to correlate the properties with change in electronegativity of the groups attached to the carbonyl bond. The bond strength increases with increase of electronegativity of these groups partly directly because they increase the effective electronegativity of the carbon atom of the C⁼⁼O group, and partly indirectly because they reduce the bond polarity: it would be difficult to try to separate the two effects.

The Overlap of Atomic Orbitals.—Other things being equal, the greater the overlap of atomic wave functions the greater the strength of the resulting molecular orbital: this is a reason, for example, why π bonds in double and triple bonds are weaker than σ bonds—for the "sideways" overlap of $p\pi$ electrons is less than the "endwise" overlap of $p\sigma$ ones. The principle of "maximum overlapping" is fundamental to both the electron-pair bond and the molecular orbital theory of valency.

Increase of electronegativity of bonded atoms increases the bond strength—but only up to a point. The 2*p* distributions contract inwards towards the nucleus as we pass from N to O to F. Thus, as the electronegativity of bonded atoms increases, there must come a time when, in order to secure appreciable overlap of the atomic wave functions, the atoms must be so close together that appreciable repulsion of the nuclei is likely to result. In other words, beyond a certain point, increase of electronegativity of X in a bond X–X may weaken rather than strengthen the bond.

We only expect to find cases of reduced strength due to reduced overlap in bonds to highly electronegative atoms. We now consider three examples.

(1) *Bond strengths in peroxides.* The author has pointed out (*Trans. Faraday Soc.*, 1946, **42**, 264) that the variations in OO bond strength from molecule to molecule can partly be understood in terms of charge transfer effects established by the study of the ionisation potentials of non-bonding electrons in alkyl halides. The greater the negative charge transfer to the OO group, apparently the greater the OO bond strength (Walsh, this vol., p. 331). This can only be understood in terms of the electronegativity of oxygen atoms being too high to give the overlap that would correspond to the maximum OO bond strength: reduction of their effective electronegativity increases the overlap and strengthens the bond. In this way one can understand the relation between the electronegativity of an element and its tendency to form per-compounds (Walsh, *J. Chem. Physics*, 1947, **15**, 688).

Similarly, it is significant that the NN bond (64 kcals. in N_2H_4) is weaker than the NH (93 kcals. in NH_3), the OO (64 kcals. in H_2O_2) is weaker than the OH (110 kcals. in H_2O), and the FF (64 kcals. in F_2) weaker than the FH (148 kcals. in HF). In all these cases the electronegativity product is greater and the bond polarity is less in XX than in XH. That XX is weaker than XH must therefore be ascribed to a third factor affecting bond strength and this factor we identify with the overlap of atomic orbitals. The interplay of electronegativity product and

overlap keeps the NN bond of N_2H_4, the OO bond of H_2O_2 and the FF bond of F_2 remarkably similar in length, force constant, and bond energy. That the CC bond in ethane is markedly stronger than the NN bond in hydrazine (~95 and ~64 kcals., respectively) is also to be explained as partly due to reduced overlap in the NN bond, though another factor operating here is doubtless the peculiarities of hybridisation. The NN bond of N_2O_4 is even weaker than that of N_2H_4, a fact readily explicable as due to the very high dipoles in the NO_2 groups (Walsh, *J. Chem. Physics, loc. cit.*).

(2) *Halogen compounds.* It is a striking fact that the compound ClF has a greater bond strength (86·5 kcals.) than has F_2 or Cl_2 (64 and 58 kcals., respectively).* The bond strength increase in the series I_2, Br_2, Cl_2, F_2 can be attributed to increase of the electronegativity product in this series, but the FF strength is less than one would expect on this basis, knowing the big jump of electronegativity from Cl to F. The FF strength is probably partly reduced because of reduced overlap consequent upon too great an electronegativity. Replacement of one of the fluorine atoms by Cl enables this overlap to increase and so causes an increase of bond strength, in spite of a polarity effect and a reduced electronegativity product.

(3) *Glyoxal and related compounds.* The conjugation of the two C=O groups in glyoxal should result in a strengthening of the central CC bond relative to ethane, and calculations by Coulson (*Trans. Faraday Soc.*, 1946, **42**, 106) support this expectation. Nevertheless, photochemical data for diacetyl show that the central CC is more easily broken than is that of ethane. The indications are therefore that the CC dissociation energy of glyoxal is less than that of ethane. Even if E(CC) in glyoxal should be greater than D(CC), one is led to the conclusion that there is some factor that offsets the increased strength due to conjugation in glyoxal.† This factor we identify with small σ electron overlap in the CC bond. The small overlap is consequent upon the small size of the carbon orbitals involved, due to the high electronegativity. It is understandable therefore that r(CC) may be as low as $1{\cdot}47 \pm 0{\cdot}02$ A. (the electron-diffraction value) without corresponding to high CC strength. Coulson's calculations do not take into account variation in the bond order of σ CC bonds. If this explanation be true, E(CC) in diacetyl may be greater than E(CC) in glyoxal. Oxalyl chloride should have a lower CC bond strength than glyoxal, in accord with its ready photochemical decomposition and its use by Kharasch and his co-workers as a source of radicals (Waters, *op. cit.*, p. 189). Cyanogen and oxalic acid may prove to be other molecules with a lower CC bond order than simple conjugation theory would expect.

Gordy emphasized the importance of electronegativity, but neglected atomic orbital overlap, in determining bond strength. It is not therefore surprising that his relation fails for H_2O_2 and probably for F_2. It does not account for the increase of strength in FCl relatively to F_2, unless the bond-order term in his expression is specifically related to overlap. Pauling has emphasized the importance of atomic orbital overlap, but has neglected that of electronegativity. As a result, his work (" Nature of the Chemical Bond," Cornell, 1940, p. 86) would lead one to expect that the strength of CH bonds would increase in the series $C_2H_2 < C_2H_4 < C_2H_6$, because the greater the proportion of p character in a hybrid valency, the better can that valency orbital overlap with another atomic orbital. In fact, the CH bond strengths increase in the opposite order, which is explicable as above in terms of varying carbon electronegativity.

Repulsion of Parallel Filled Orbitals.—The fact that the oxygen molecule has two unpaired electrons in its ground state can be reconciled with the pair-bond theory if we make the simple assumption that pairs of electrons in parallel filled atomic orbitals repel each other strongly. This repulsion is the analogue on the pair-bond theory of the " anti-bonding orbitals " of the molecular orbital theory. Suppose the $2p_z$ atomic orbitals overlap to form the first or σ bond. As a result of the repulsion, one oxygen atom twists relatively to the other so that the configuration of one may be written $2p_x^2\ 2p_y\ 2p_z$, and of the other $2p_x\ 2p_y^2\ 2p_z$. This means that repulsion of the parallel lone pairs is avoided, being replaced by the *attractive* interaction of a single electron with a parallel lone pair. A state of the oxygen molecule with two unpaired electrons has thus lower energy than the state represented by the diagram O=O.

The same hypothesis—repulsion of filled parallel orbitals—explains the skew nature of H_2O_2: again, twisting occurs to minimise the repulsion. In a peroxide where twisting is partly prevented by steric factors, the OO strength must be reduced from the value that would otherwise prevail. Di-*tert.*-butyl peroxide probably supplies an example (Walsh, this vol., p. 331).

* Gaydon (" Dissociation Energies ", Chapman and Hall, 1947) favours a value 60·3 for D(FCl) and a consequent value considerably below 64 kcals. for $D(F_2)$.

† This conclusion is confirmed by considerations based upon the measured angles of the molecule and hybridisation theory (Coulson, V. Henri Memorial Vol., Desoer, Liége, in the press).

Repulsion of parallel filled orbitals must be an important factor reducing the bond strength in Cl_2 or in F_2. This is the pair-bond theory analogue of the molecular-orbital theory description of these molecules as containing electrons in anti-bonding orbitals. On either theory, removal of one of the non-bonding electrons should result in an increase of bond strength—an expectation strikingly confirmed by the facts, since the fundamental vibrational frequencies for Cl_2 and Cl_2^+ are 565 and 645 cm.$^{-1}$, respectively (Herzberg, 1939, *loc. cit.*).

Repulsion of adjacent filled atomic orbitals occurs in the carbon tetrachloride molecule (Walsh, *Trans. Faraday Soc.*, 1947, **43**, 158). It probably occurs also in carbon tetrafluoride. In the silicon tetrahalides the much larger size of a silicon than of a carbon atom reduces these repulsions and so

$$E(\text{Si–Cl})_{SiCl_4} = 90, \text{ whereas } E(\text{C–Cl})_{CCl_4} = 83 \text{ kcals.}$$

and

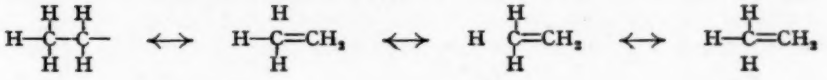
$$E(\text{Si–F})_{SiF_4} = 147, \text{ whereas } E(\text{C–F})_{CF_4} = 120 \text{ kcals.}$$

[the latent heats of sublimation of C and Si to their valency states being assumed to be respectively 190 (Long and Norrish, *loc. cit.*) and 102 kcals. (Skinner, 1945, *loc. cit.*)], in spite of the lowered electronegativity of Si relatively to C. Other molecules in which this repulsion of filled atomic orbitals is important comprise *o*-dichlorobenzene, the various halogenated methanes, ethanes, and ethylenes, and the acetyl halides (Walsh, *Trans. Faraday Soc.*, 1947, **43**, 158).

It is clear, therefore, that in assessing probable bond strengths it is always important to consider the pair-bond theory viewpoint of possible repulsion of parallel filled atomic orbitals.

Stability of Fission Fragments.—This is a factor affecting dissociaton, rather than bond, energies. In general the stability of any group X will not be the same in the free state as in the compounds X–H or X–X. If the stability is less in the free state, then $D(\text{X–X}) > E(\text{X–X})$ or $D(\text{X–H}) > E(\text{X–H})$: an example is provided by HO–H. If the stability is greater in the free state, then $D(\text{X–X}) < E(\text{X–X})$: examples are provided by HO–OH and CH_3–CH_3. Further examples are to be seen in those compounds where fission of a bond increases the space available for " delocalisation " of π electrons. Thus if a CH bond in the methyl group of propylene is broken, the carbon atom of the resulting $^-CH_2$ assumes the free methyl configuration, *i.e.*, becomes planar with one electron in (originally) a $2p\pi$ orbital at right angles to the plane. This $2p\pi$ orbital must overlap with the π orbital of the double bond, so that the three π electons come to occupy orbitals extending over all three carbon atoms. The effect of this is to lower the energy of the free allyl group relatively to its energy in the propylene molecule. The lowering may be referred to as the resonance energy of the allyl radical. Its effect is to alter the dissociation energy of the allyl–H bond, but not necessarily to affect the bond energy.

Resonance in radicals of the allyl type is very strongly founded in quantum-mechanical theory and there is much evidence to show that it is important quantitatively as well as qualitatively. For example, when a free allyl-type radical is formed, products derived from the two forms —CHR—CH=CH_2 and CHR=CH—CH_2— appear. It should be regarded as resulting fundamentally from the overlap of atomic *p* orbitals to give inevitably non-localised molecular orbitals. Some workers have supposed resonance to occur in alkyl radicals, for example



increasing in the series

$$\text{Me} < \text{Et} < \text{Pr}^i < \text{Bu}^t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and have supposed the decreases in dissociation energy in the series

$$\text{Me–X, Et–X, Pr}^i\text{–X, Bu}^t\text{–X} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

to be attributable to this cause. This type of resonance is much less strongly founded in theory and experiment. It does not correspond to overlap of atomic orbitals with consequent delocalisation of molecular orbitals in the way that does resonance in, say, the benzene molecule or the allyl radical. Nor—if it be granted as likely to occur—is there compelling evidence of its being quantitatively important. One of the main qualitative reasons for supposing it—the decrease of *D* in the series (3)—has been removed with the realisation that the bond polarity C–X increases in this series and that increase of polarity means weakening of bond strength. Since the ionisation potential of the odd electron does not increase but decreases in the series (2), the alkyl resonance theory has necessitated the further *ad hoc* postulate that resonance in the positive ion increases even more rapidly in series (2) than does resonance in the radical. Further,

the theory is not based upon any discussion of the energy that would be necessary to distort the tetrahedral bond angles in (III) and the trigonal angles in (IV) to intermediate positions in

(III.) (IV.)

which resonance might be possible: in fact, resonance would only occur if this distortion energy were less than the resonance energy possible after distortion. Unless further evidence is forthcoming, the theory of the importance of resonance in alkyl radicals as a determining factor for dissociation energies should be treated with reserve.

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95. *Excited States of Benzene. Part I. Introductory Consideration of Some Spectral Properties of Vibrations accompanying Electronic Transitions of Benzene and Deuterated Benzenes.*

By FRANCESCA M. GARFORTH, CHRISTOPHER K. INGOLD, and HARRY G. POOLE.

Previous investigations (" Structure of Benzene ", Parts I—XXI, *J.*, 1936 and 1946) having provided some knowledge of the geometry and dynamics of the electronic ground state of the benzene molecule, attention is now turned to the first electronically excited state. This can be studied with respect to its vibrations, not directly as the ground state can, but only in admixture with the ground state, through the joint effect of the vibrations of both states on the vibrational structure of transitions between the ground and the excited state. In this introductory paper, the principles underlying the work are explained, and some of the more useful relevant results of the application of general spectroscopic theory are given. The experimental material consists in the near-ultraviolet absorption and fluorescence band systems of benzene, hexadeuterobenzene, and certain partly deuterated benzenes with oriented deuterium atoms: a number of such spectra are described for the first time. The evaluation of this material (Parts II—X) involves vibrational analyses extended to cover large numbers of bands which are not amongst the strongest in the spectra. Taking account of existing knowledge of vibrations of the ground state, fundamental frequencies have been assigned to many vibrations of the electronically excited molecules. In the course of the analysis, and for the purpose of obtaining upper-state fundamental frequencies which cannot be directly observed, extensive use is made (Part XI) of the principle that isotopic substitution does not change the internal force-field of a molecule in any given electronic state. The results of this study of upper-state frequencies are employed (Part XII) in order to calculate the dimensions, force-system, and zero-point energies of the excited molecules; and it is the first time in the study of band-spectroscopy that such a set of conclusions has been derived for any excited polyatomic molecule.

(1) *Scope.*—The study of the vibrations and force system of the electronic ground state of benzene is now sufficiently advanced to assist the pursuit of similar problems relating to the excited electronic states of this molecule. In these papers it is proposed to develop such studies. The observational material consists in ultraviolet absorption and emission spectra, dependent on transitions between the electronic ground state and various electronically excited states of benzene in its several isotopically modified forms.

We take up this subject for two reasons. First, benzene was the starting point of, and is the most fully studied example in, the rapidly developing, modern theory of the relation between the colour and structure of organic compounds: it is likely to retain a fundamental position in that theory.

Secondly, with reference to the study of spectroscopy for its own sake, the present position is that the principles underlying the analysis of the electronic spectra of atoms and diatomic molecules are fully known, that the vibration and rotation spectra of diatomic and polyatomic molecules are also in principle fully understood, but that the electronic spectroscopy of polyatomic molecules is still in its exploratory stages; and benzene, with its high symmetry and practical possibilities of isotopic modification, is an almost ideal example with which to develop this branch of spectroscopy.

In the present papers considerable use is made of both the mentioned properties of the benzene molecule. With their help we achieve the first determination of a force system of an electronically excited polyatomic molecule. New observations are provided on the absorption and fluorescence spectra of deuterated benzenes. Brief preliminary accounts of the investigation have already been given (*Nature*, 1946, **157**, 46; **158**, 163).

(2) *Electronic States and Transitions of Benzene.*—Benzene has the symmetry D_{6h}, *i.e.*, a 6-fold axis, a perpendicular 2-fold axis, and a centre, plus such other symmetry as this implies. When thinking of the electronic motion, and therefore of nuclear charges but not of nuclear masses, we shall write this symmetry $\mathbf{D_{6h}}$. This is because the nuclear charges control the electronic motion, the forms of which we shall symbolise by means of heavy type (italics being reserved, as heretofore, for the representation of nuclear motion). Just as with nuclear motion, so also with electronic motion, the possible forms can be classified according to what symmetry they preserve. The 12 classes, 8 non-degenerate (**A**, **B**) and 4 doubly degenerate (**E**), are symbolised $\mathbf{A_{1g}}$, $\mathbf{A_{1u}}$, $\mathbf{A_{2g}}$, $\mathbf{A_{2u}}$, $\mathbf{B_{1g}}$, $\mathbf{B_{1u}}$, $\mathbf{B_{2g}}$, $\mathbf{B_{2u}}$, $\mathbf{E_g^+}$, $\mathbf{E_u^+}$, $\mathbf{E_g^-}$, $\mathbf{E_u^-}$. Here, **A** connotes 6-fold, **B** 3-fold, + 2-fold, and — 1-fold symmetry about the z-axis (normal to the ring), **1** means 2-fold, and **2** 1-fold symmetry about the y-axis (through para-atoms), whilst **g** signifies symmetry and **u** antisymmetry relative to the centre. These symbols refer to the total electronic orbital wave function, just as the corresponding italic symbols relate to the total nuclear vibrational wave function (as well as to the normal co-ordinate in the special case of a fundamental vibration).

Actually, the above 12 symmetry classes do not all contain electronic states, just as the symmetry classes for nuclear motion do not all contain fundamental vibrations (see *J.*, 1946, 227, especially Table VII). It can be shown, by a simple application of symmetry theory, that non-ionised benzene, because of the even number of its electrons, cannot have electronic states which are antisymmetrical with respect to the molecular plane. This reduces the list of symmetry classes which are available for occupation by electronic states to the six following: $\mathbf{A_{1g}}$, $\mathbf{A_{2g}}$, $\mathbf{B_{1u}}$, $\mathbf{B_{2u}}$, $\mathbf{E_g^+}$, $\mathbf{E_u^-}$.

The electronic ground state of benzene is a singlet state, and therefore only singlet states will participate in the stronger transitions involving the ground state. We shall be concerned only with singlet states, and therefore have no need to introduce a symbol for the electronic spin. Nor shall we have to concern ourselves with the electronic spin wave functions.

Benzene has several ultraviolet absorption systems. The first runs out from about 2600 A., and it is with the detailed study of this that our investigation commences. A stronger system starts at about 2000 A., and this is overlapped by a still stronger one at about 1850 A. After that two Rydberg series appear, which run out to a common limit at 1350 A.

Hückel first discussed the lower electronic states of benzene as molecular states of the six unsaturation electrons; and his work has been brilliantly developed by Sklar. The six atomic orbitals, $2p\pi$, of these electrons combine to produce the following molecular orbitals, in order of increasing energy: $\mathbf{2a_{2u}}$, $\mathbf{2e_g^-}$, $\mathbf{2e_u^+}$, $\mathbf{2b_{2g}}$. The symmetry symbols have the meanings given, except that, by custom, lower-case letters are used for single-electron wave-functions. The prefix 2 refers to the principal quantum number. Pauli's principle allows the $\mathbf{a_{2u}}$ and $\mathbf{b_{2g}}$ shells each to accommodate two, and the degenerate $\mathbf{e_g^-}$ and $\mathbf{e_u^+}$ shells four, electrons. The ground state, formed by filling the $\mathbf{2a_{2u}}$ and $\mathbf{2e_g^-}$ shells, has the symmetry $(\mathbf{a_{2u}})^2(\mathbf{e_g^-})^4 = \mathbf{A_{1g}}$. The lowest excited states are obtained by promoting a $\mathbf{2e_g^-}$ electron to a $\mathbf{2e_u^+}$ orbital. Two non-degenerate states and one degenerate state thus arise, which have the symmetries $(\mathbf{a_{2u}})^2(\mathbf{e_g^-})^3(\mathbf{e_u^+}) = \mathbf{B_{2u}}$, $\mathbf{B_{1u}}$, $\mathbf{E_u^-}$. These symmetry relations are readily verified by multiplying together the appropriate sets of operators (as given, *e.g.*, in Table VII, *J.*, 1946, 227). According to Sklar's calculations of the energy relationship, the $\mathbf{B_{2u}}$ state lies the lowest of these three (*J. Chem. Physics*, 1937, **5**, 669). Goeppert-Mayer and Sklar's further calculations place the $\mathbf{B_{1u}}$ state higher, and the $\mathbf{E_u^-}$ state higher still on the energy scale (*ibid.*, 1938, **6**, 645). Revised calculations by A. London give the same order (*ibid.*, 1945, **13**, 396). Neither the $\mathbf{B_{2u}}$ nor the $\mathbf{B_{1u}}$ state has the symmetry of a component of the electric moment, and therefore transitions between the ground state and each of these states are forbidden. On the other hand, the $\mathbf{E_u^-}$ state has the symmetry of an x- or y-component of the electric moment, so that transitions between the ground state and this state are allowed.

Sklar first assigned (*loc. cit.*) as a $\mathbf{B_{2u}}$ state the upper state of the transition starting near 2600 A. Though the transition would in this case be forbidden under the equilibrium symmetry of the nuclear system, it would be able to occur, when, in either of the interacting states, the molecular symmetry became suitably reduced by an appropriate nuclear vibration. Goeppert-Mayer and Sklar (*loc. cit.*), and also Nordheim, Sponer, and Teller (*ibid.*, 1940, **8**, 455), assigned the absorption system starting around 2000 A. as a forbidden transition to a $\mathbf{B_{1u}}$ state, and the strong absorption system beyond 1850 A. as an allowed transition to an $\mathbf{E_u^-}$ state.* The last-named

* Probably this state is the one of chief importance for the polarisability (refractive index) of benzene, not the state involved in the 2600 A. transition, as supposed by Ingold, Raisin, and Wilson (*J.*, 1936, 915).

authors supposed the Rydberg series to arise by excitation of the same loosely held $\mathbf{e}_g^-$ electron to orbitals with principal quantum numbers higher than 2.

(3) *Selection Rules for Vibrations involved with Electronic Transitions of Benzene.*—The general selection rules for the vibrational changes that may accompany an allowed electronic transition were given by Herzberg and Teller (*Z. physikal. Chem.*, 1933, *B*, **21**, 410). In the case in which the equilibrium symmetries of the nuclear system in the upper and lower electronic states are identical, the quantum numbers of the totally symmetrical vibrations should be the principal ones to change. Thus one expects, accompanying the 0—0 band, strong progressions, 0—1, 0—2, 0—3, . . . , in these vibrations. Progressions in upper-state vibrations should predominate in absorption, whilst progressions in lower-state vibrations should be the most important in fluorescence. We must also expect that sequences involving transitions 1—1, 2—2, . . . , *n*—*n*, . . . , in all the non-totally symmetrical vibrations will be prominent in both absorption and fluorescence, except in so far as these bands are weakened by the Boltzmann factors of their initial vibrational levels. As weak frequencies we might observe such as depend on even changes of quantum number in non-totally symmetrical vibrations, *e.g.*, transitions 0—2, 1—3, etc., and even combinations, such as combined 0—1, 0—1 changes of pairs of non-totally symmetrical vibrations of the same symmetry class.

In a forbidden transition the 0—0 band cannot appear. Associated with the electronic change there must be a vibrational transition of such a type as will produce the perturbation which makes the electronic transition possible. For any particular type of forbidden electronic transition, the symmetry conditions which the vibrational change must fulfil in order to achieve this result are readily calculated. The simplest form of vibrational perturbation would be a one-quantum change, as in a 0—1, 1—2, . . . , or 1—0, . . . , transition of some non-totally symmetrical vibration of the right symmetry. But generally, transitions may occur when, in either or both of the interacting electronic states, such vibrations are excited with such quantum numbers that the product of all the involved vibrational wave functions has the symmetry needed to produce the perturbation. Finally, upon each vibrational transition fulfilling these conditions, all the vibrational changes which may accompany an allowed electronic transition may be superposed.

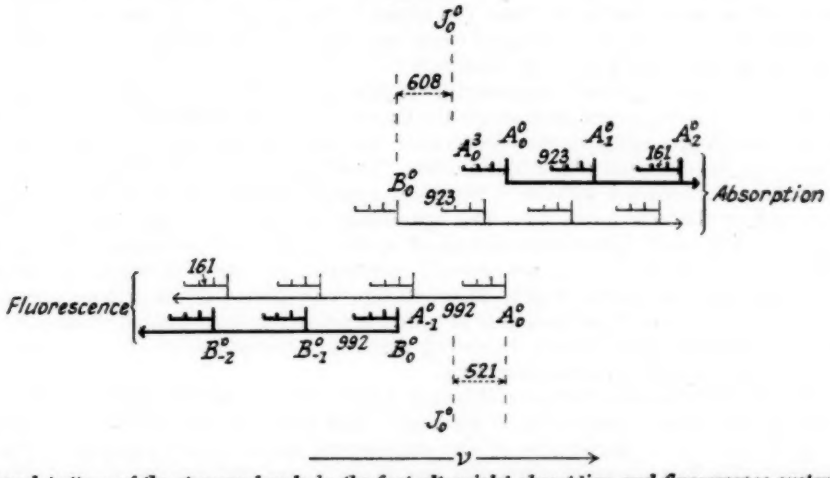
In benzene, the $\mathbf{A}_{1g}$—$\mathbf{B}_{2u}$ transition is forbidden because the product $\mathbf{A}_{1g} . \mathbf{B}_{2u}$ has not the symmetry of an electric moment, wherefore the transition moment (which is an electric moment averaged over the product of the wave functions) must vanish. Sklar pointed out (*loc. cit.*) that a vibration of E_g^+ symmetry provides a suitable perturbation, since it so operates on the product as to cause it to take on the symmetry of an electric moment in the plane of the aromatic ring: $E_g^+(\mathbf{A}_{1g} . \mathbf{B}_{2u}) = \mathbf{E}_u^- = x, y$ (as can be verified, *e.g.*, from Table XII, *J.*, 1946, 234). Amongst fundamental vibrations, an E_g^+ vibration is the only kind that can so act. Sklar assumed that, in the observed electronic transition near 2600 A., one of the four E_g^+ fundamentals provides the necessary perturbation. Sponer, Nordheim, Sklar, and Teller then showed in some detail (*J. Chem. Physics*, 1939, **7**, 207) that this theory can account very well for the salient features of the structure of the absorption and fluorescence spectra arising from this transition. The main perturbing vibration is the planar, carbon-bending, degenerate fundamental, E_g^+(C 1) (cf. Fig. 1, *J.*, 1946, 231). Its frequency, as given in the Raman spectrum of liquid benzene, is 606 cm.$^{-1}$; this, of course, applies to the electronic ground state. The absorption and fluorescence spectra themselves give the frequencies 608 cm.$^{-1}$ in the ground state and 521 cm.$^{-1}$ in the excited state.

Symmetry considerations would allow the other three E_g^+ fundamental vibrations to act in a similar way, and also any vibrational higher harmonics of E_g^+ symmetry. Furthermore, although there are no fundamental vibrations of B_{1g} symmetry, a vibrational combination tone of this symmetry could give rise to spectral activity by producing a transition moment perpendicular to the plane of the ring: $B_{1g}(\mathbf{A}_{1g} . \mathbf{B}_{2u}) = \mathbf{A}_{2u} = z$.

(4) *Main Structure of the First Ultraviolet Absorption and Fluorescence Systems of Benzene.*—The general pattern of the two related spectra is shown in a simplified form in Fig. 1. In absorption, two active origins, A_0^0 and B_0^0, 1129 cm.$^{-1}$ apart, are the starting points of progressions in the interval 923 cm.$^{-1}$, which run to higher frequencies (we call them positive), the progression starting from the higher frequency being much the stronger. In fluorescence, the same two origins are the starting points of progressions in the interval 992 cm.$^{-1}$, which run to lower frequencies (and are called negative), the progression starting from the lower frequency being much the stronger. From each band in these progressions, sequences start out: in both absorption and fluorescence they are negative; and the interval, 161 cm.$^{-1}$, is common to them all. Then (though this is omitted from Fig. 1 for simplicity), the whole of the described pattern

is repeated much more weakly with a shift of 87 cm.$^{-1}$ towards lower frequencies; that is, there is a third origin C_0^0 at this separation from A_0^0, and a fourth D_0^0 the same distance below B_0^0, each

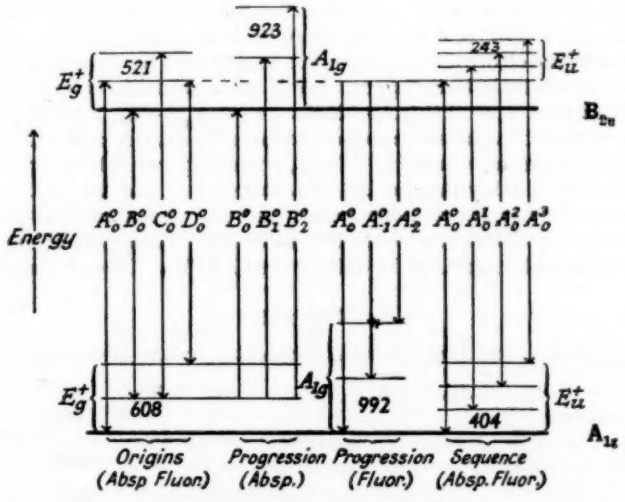
FIG. 1.



General pattern of the stronger bands in the first ultraviolet absorption and fluorescence systems of benzene vapour.

carrying the same set of progressions and sequences. We shall be concerned with many bands which do not conform to this description, which nevertheless represents the main framework of the two spectra.

FIG. 2.



Interpretation of the general pattern.

The interpretation will be clear from Fig. 2. In absorption, the origins A_0^0 and B_0^0 involve upward transitions, 0—1 and 1—0 respectively, of the perturbing E_g^+(C 1) vibration.* The second is weakened by the Boltzmann factor (0·055 at room temperature) of its initial vibrational level. Their separation is 608 + 521 = 1129 cm.$^{-1}$. The origins C_0^0 and D_0^0 involve upward transitions, 1—2 and 2—1 respectively, of the same vibration. They are both weakened, the latter very much so, by their Boltzmann factors. They lie 608 − 521 = 87 cm.$^{-1}$ below A_0^0 and B_0^0, respectively. In fluorescence, A_0^0 and B_0^0 involve downward transitions, 1—0 and 0—1

* It is therefore unnecessary to assume close-lying electronic levels as did Ingold and Wilson (*J.*, 1936, 941).

respectively, of the E_g^+(C 1) vibration. Since we are concerned with fluorescence at pressures permitting a thermal distribution of vibrational energy in the excited state, the former of these transitions will be weakened by the Boltzmann factor of its initial state. The origins C_0^0 and D_0^0 correspond, in fluorescence, to downward transitions, 2—1 and 1—2 respectively, and therefore the former will be weakened more than the latter. The positions of the four active origins evidently determine that of the forbidden electronic origin, J_0^0, as well as the values of the two frequencies of the perturbing E_g^+(C 1) vibration.

The main progressions depend on quantum changes in the totally symmetrical ring-breathing vibration A_{1g}(C). Its frequency, as given in the Raman spectrum, is 992 cm.$^{-1}$. Its frequencies, as given by the progressions in the ultraviolet spectra, are 992 cm.$^{-1}$ in the ground state and 923 cm.$^{-1}$ in the electronically excited state. In absorption, positive progressions (Fig. 2) in the excited state frequency, 923 cm.$^{-1}$, involving upward transitions, 0—1, 0—2, 0—3, . . . , start from each of the active origins. The beginnings of negative progressions in the ground state frequency, 992 cm.$^{-1}$, can also be discerned on the plates, but the bands, which arise from upward transitions, 1—0, . . . , are greatly weakened by their Boltzmann factors. In fluorescence, negative progressions (Fig. 2) in 992 cm.$^{-1}$, involving downward transitions, 0—1, 0—2, . . . , predominate. The beginning of positive progressions in 923 cm.$^{-1}$ can also be seen on the plates, but these bands, which depend on downward transitions, 1—0, . . . , are likewise greatly weakened by their Boltzmann factors.

Kistiakowsky and Solomon first established (*J. Chem. Physics*, 1937, **5**, 609), by measurements on the temperature-dependence of band intensity, that the sequences in 161 cm.$^{-1}$ arise from 1—1, 2—2, 3—3, . . . , transitions of the degenerate, out-of-plane vibration E_u^+(C). The frequencies of this fundamental vibration are much lower than those of any other. The ground-state frequency, as given by the Raman spectrum of liquid benzene, is 405 cm.$^{-1}$. As will appear in Part II, the absorption and fluorescence spectra of benzene vapour give 404 cm.$^{-1}$ for the frequency of this vibration in the electronic ground state, and 243 cm.$^{-1}$ for its frequency in the excited state. The difference 404 − 243 = 161 cm.$^{-1}$ forms the sequence interval common to the absorption and fluorescence spectra, in both of which the sequence must obviously run in the negative direction (Fig. 2). In principle, all vibrations can produce such sequences. But the outstanding persistence of the sequences of this vibration is clearly due largely to the fact that its frequencies are so low, and that therefore its Boltzmann factors—at room temperature, $(0{\cdot}14)^n$ for n quanta in the electronic ground state, and $(0{\cdot}31)^n$ for n quanta in the excited state—are not too serious an obstacle to its appearance in n—n transitions up to several quanta.

(5) *More Detailed Statement of Selection Rules for the* $\mathbf{A_{1g} - B_{2u}}$ *Transition of* D_{6h} *Benzenes.*—The D_{6h} benzenes with which we shall be concerned are ordinary benzene and hexadeuterobenzene. Each has ten non-degenerate vibrations (A, B), including two which are totally symmetrical (A_{1g}), and a further ten doubly degenerate vibrations (E). The whole twenty are distributed among ten symmetry classes, six non-degenerate and four degenerate, as shown in Table I. A complete set of fundamental frequencies for the electronic ground state of each of these molecules has been given by Herzfeld, Ingold, and Poole (*J.*, 1946, 316). These frequencies are reproduced in Table I.

TABLE I.

Vibrations of D_{6h} *Benzenes and Fundamental Frequencies in the Electronic Ground State* (*cm.*$^{-1}$).

	Symmetry:	A_{1g}.	A_{2g}.	A_{2u}.	B_{1u}.	B_{2g}.	B_{2u}.	E_g^+.	E_u^+.	E_g^-.	E_u^-.
C_6H_6	(C) (1)	992			1010	703	1648	606	405		1485
	(C) (2)							1596			
	(H) (1)	3062	1326	671	3060	985	1110	3047	970	849	1037
	(H) (2)							1178			3080
C_6D_6	(C) (1)	943			963	601	1571	577	352		1333
	(C) (2)							1551			
	(H) (1)	2293	1037	496	2290	827	825	2265	793	662	813
	(H) (2)							867			2294

The general selection rule for vibrations accompanying the $\mathbf{A_{1g}—B_{2u}}$ electronic transition of a D_{6h} benzene is that, in either or both of the combining states, such vibrations may be excited

with such quantum numbers that the product of all the involved vibrational wave functions has either the symmetry E_g^+, or the symmetry B_{1g} (cf. Section 3). Some consequences of this rule are contained in Table II (which can be deduced from Table XII, *J.*, 1946, 234).

TABLE II.

Vibrations allowed in Combination with the $\mathbf{A_{1g}}$—$\mathbf{B_{2u}}$ *Transition of a* D_{6h} *Benzene.*

$\psi'_{\text{vib.}} \cdot \psi''_{\text{vib.}}$	E_g^+ (perp. bands).		B_{1g} (par. bands).
One quantum (either state)	** E_g^+		—
Two quanta (same or different states)	** E_g^+, A_{1g} E_g^+, A_{2g} E_u^+, A_{2u} E_u^-, B_{1u} E_g^-, B_{2g} E_u^-, B_{2u}	† E_g^+, E_g^+ † E_g^-, E_g^- † E_u^+, E_u^+ † E_u^-, E_u^-	A_{2g}, B_{2g} A_{2u}, B_{2u} E_g^+, E_g^- E_u^+, E_u^-
One E_g^+ and two other quanta (same state or distributed)	** E_g^+, A_{1g}, A_{1g} * ,, , A_{2g}, A_{2g} * ,, , A_{2u}, A_{2u} * ,, , B_{1u}, B_{1u} * ,, , B_{2g}, B_{2g} * ,, , B_{2u}, B_{2u} * ,, , E_g^+, E_g^+ * ,, , E_u^+, E_u^+ * ,, , E_g^-, E_g^- * ,, , E_u^-, E_u^-	E_g^+, A_{2g}, A_{1g} ,, , B_{2u}, B_{1u} ,, , E_g^+, A_{1g} ,, , E_g^+, A_{2g} ,, , E_u^+, A_{2u} ,, , E_u^-, B_{1u} ,, , E_g^-, B_{2g} ,, , E_u^-, B_{2u}	E_g^+, E_g^-, A_{1g} ,, , E_g^-, A_{2g} ,, , E_u^-, A_{2u} ,, , E_u^+, B_{1u} ,, , E_g^+, B_{2g} ,, , E_u^+, B_{2u} ,, , E_g^+, E_g^- ,, , E_u^+, E_u^-

This table gives the allowed excitations of one, two, and certain sets of three, vibrational quanta: they may be distributed in any manner between the two combining states. The entries marked **, which involve a single E_g^+ quantum, and, apart from this, only totally symmetrical quanta, represent bands which may appear strongly, although, in particular cases, a low transition probability, or a small Boltzmann factor applying to the vibrational energy level of the initial state, may reduce the spectral intensity. The development of strong bands is illustrated by the production of the active origins A_0^0 and B_0^0, and of the totally symmetrical A_{1g}(C) progressions of the upper or lower electronic state, which in absorption or fluorescence proceed from these origins. Table II has been carried far enough to cover only the first three members of each such progression, but the principles on which it could be extended are clear.

The entries marked *, which involve, besides a single E_g^+ quantum, two non-totally symmetrical quanta of identical symmetry, represent bands which, with the same limitations as before, may appear strongly in a special case, though not in the general case. The special case is that in which identically the same vibration is excited with one quantum in each of the combining states. Illustrations are provided by the 1—1 bands of the already mentioned sequences, due to n—n transitions of the vibration E_u^+(C), which start from each of the stronger bands of the A and B progressions. Table II is carried far enough to cover only the 0—0 and 1—1 bands of such sequences, but, again, the principles on which it could be extended are obvious.

Included under the same set of entries are the transitions in which two quanta of the same non-totally symmetrical vibration are present in one of the combining states. Such transitions belong in principle to the category of weak transitions; but since two like quanta jointly possess total symmetry, we may expect that the bands will often be comparatively prominent among the weaker bands of the absorption and fluorescence spectra. Many such bands will be pointed out in the following papers. They appear in positions displaced from A_0^0 or B_0^0, or from other strong bands of the A and B progressions, by the frequency of the first overtone of the vibration concerned, the displacement being towards long waves if the overtone frequency belongs to the electronic ground state, and towards short waves if the frequency belongs to the upper electronic state.

The entries marked † have the following special feature. It is a property of degenerate

vibrations that two quanta of the same symmetry class can in combination always produce the symmetry E_g^+ : no non-degenerate vibrations behave in this way (cf. Table XII, *J.*, 1946, 234). It follows that the presence, either in the same state or in different states of a possible transition, of two degenerate quanta of the same symmetry class, in particular, two quanta of the same degenerate vibration, is sufficient to permit the transition. An important case is that in which the same degenerate vibration is present with one quantum in each electronic state. Thus the 1—1 transition of any degenerate vibration is allowed, there being no need for the excitation of an additional E_g^+ quantum, or for any other equivalent combination of vibrations, in order to confer spectral activity. The same is true if two quanta of the same degenerate vibration are present in each state. Thus the 2—2 transition of any degenerate vibration is also allowed, and need not be accompanied by any other vibrational change. The result may be generalised. It follows that sequences due to n—n transitions of degenerate vibrations may run, not only from A_0^0 and B_0^0 and from the other bands of the A and B progressions, but also from the forbidden electronic origin, except, of course, that in this last case the 0—0 band of the sequence will be missing. For example, an E_u^+(C) sequence with a missing 0—0 band is always found in association with the electronic origin. Conversely, the recognition of a sequence in this position, or even of the 1—1 band of such a sequence, will immediately show that the responsible vibration is degenerate.

A similar rule applies if two degenerate quanta of the same symmetry class, in particular, two quanta of the same degenerate vibration, are present in one of the combining states. In this case the transition is only weakly allowed; but it is still true that no additional E_g^+ vibration, or combination of vibrations, need be present in order to confer spectral activity. Thus, in the case of degenerate vibrations, we may expect weak bands displaced, not only from A_0^0 and B_0^0 and from the main bands of the A and B progressions, but also from the forbidden electronic origin, by the frequency of the first overtone of the vibration concerned: such bands will be displaced towards long waves if the vibration is in the lower electronic state and towards short waves if it is in the upper state. A number of examples of overtone bands, which, by appearing in positions displaced by the overtone frequency from the forbidden origin, as well as from strong bands, confess themselves to belong to a degenerate vibration, will be found in the accompanying papers.

The unmarked entries in Table II represent transitions which are in principle weak; but, in the case of weakly allowed perpendicular bands only (cf. the centre column of the Table), the following cause may lead to a somewhat strong appearance of certain bands. It is well established that when any two non-orthogonal vibrational states, such as a fundamental and either an overtone of another vibration or a combination tone of two other vibrations, have identical symmetry and nearly the same frequency, a mutual perturbation, or resonance, may arise, which results in a certain amount of mixing of the wave functions, accompanied by limited displacements of the frequencies. It follows that, if the frequency of a vibrational level of a state which, in transitions with a second state, produces a weakly allowed perpendicular band happens to lie close to the frequency of a vibrational level of the first state which, in transitions with identically the same second state, produces a strong perpendicular band, then these two transitions may become mixed together, with the result that the weakly allowed band may in fact appear somewhat strongly, having acquired intensity at the expense of the neighbouring strong band. As the accompanying papers show, examples of band intensification through resonance are common in the electronic spectra of benzenes—quite as common as in the Raman and infra-red spectra, in which the resonance phenomenon has been mainly illustrated hitherto.

Parallel bands cannot be intensified in a similar manner, simply because the symmetry condition for resonance must be fulfilled, and there are no strong parallel bands from which any weak ones could gain intensity.

(6) *Vibrational Selection Rules for the* $\mathbf{A_{1g}}$—$\mathbf{B_{2u}}$ *Transition of* D_{3h} *Benzenes.*—The only benzene of this type with which we shall be concerned is 1 : 3 : 5-trideuterobenzene. Its symmetry is $\mathbf{D_{6h}}$ with respect to nuclear charges, but only D_{3h} with respect to nuclear masses.*

In such benzenes the electronic transition is, of course, still forbidden for itself, though it becomes allowed in the presence of a deforming vibration having the right symmetry properties. The vibration must have the symmetry properties of one of the classes E_g^+ and B_{1g} of the group D_{6h} in respect of all those symmetry elements of the group D_{6h} which are preserved in its subgroup D_{3h} (cf. *J.*, 1946, 224). Our discussion of the D_{6h} benzenes (Section 3) shows that this condition is necessary: in order to see that it is sufficient one has only to reflect that a vibration

* This is not strictly true, because of the finite mass of the electrons; but it is a very close approximation.

cannot have the " wrong " symmetry properties, *i.e.*, those which would cause a cancellation of the transition moment, with respect to elements of symmetry that do not exist in the D_{3h} group. The symmetry classes of the D_{3h} group which have the required symmetry properties are E', and A_1''. Vibrations of the former type can give perpendicular bands, *i.e.*, bands whose transition moments lie in the plane of the molecule. Vibrations of the latter type could produce parallel bands, *i.e.*, those whose transition moments are normal to the plane of the ring. 1 : 3 : 5-Trideuterobenzene has seven fundamental vibrations of the symmetry class E', and in principle a single quantum of any one of these, in either of the combining states, would be sufficient to permit transition. It has no fundamental vibration belonging to the symmetry class A_1'', although vibrational combinations exist which collectively possess this symmetry.

As with the D_{6h} benzenes, so also with the D_{3h} benzene, the observed band systems of the absorption and fluorescence spectra depend overwhelmingly on the perturbing effect of one vibration. This is the degenerate, carbon-bending vibration, which we shall call E'(C 1), since it is very closely similar to the D_{6h} vibration E_g^+(C 1), to which the stronger bands of the spectra of benzene and hexadeuterobenzene are due. Changes by one quantum in this E'(C 1) vibration of 1 : 3 : 5-trideuterobenzene produce the four active orgins, A, B, C, and D, of the absorption and fluorescence spectra, just as described in Section 4, the general spectral pattern being closely similar to that already illustrated in the case of the D_{6h} molecules.

As before, the main progressions, positive in absorption and negative in fluorescence, must depend on quantum changes, unrestricted by symmetry, in totally symmetrical vibrations. We saw that, in the absorption and fluorescence spectra of the D_{6h} benzenes, all the stronger progressions depended on changes in the quantum number of the totally symmetrical carbon vibration, A_{1g}(C). In the D_{3h} benzene there are two totally symmetrical carbon vibrations, which are closely similar. That which has the lower frequency, and which appears more strongly in the Raman effect, we shall call A_1'(C) : in it, most of the synchronous radial motion is in the CD-groups. The other, which has a slightly higher frequency, and appears with somewhat less intensity in the Raman spectrum, we call A_1'(C') : here most of the swelling motion is in the CH-groups. The general difference between the progressions of the D_{6h} benzenes and those of the D_{3h} benzene will therefore consist in this, *viz.*, that, in place of any given A_{1g}(C) progression of a D_{6h} benzene, we may expect to find overlapping progressions in A_1'(C) and A_1'(C'), as well as mixtures of the two. Guided by the Raman intensities, which largely reflect the ring-swelling character of these vibrations, we may expect the progression of higher frequency to be rather weaker than the other.

In the spectra of D_{6h} benzenes, each of the stronger bands of the main progressions was found to be the starting point of a negatively-running sequence, due to the superposition of 1—1, 2—2, . . . , transitions of the low-frequency vibration, E_u^+(C), on the other vibrational changes. Similarly, in the spectra of the D_{3h} compound, the stronger bands of the main progressions start sequences involving n—n transitions of a closely similar vibration, which we shall call E''(C). The repeating frequency interval in such sequences corresponds to the difference between the fundamental frequencies of the vibration in the lower and upper electronic states.

For the purpose of discussing the weaker frequencies which appear in the absorption and fluorescence spectra of 1 : 3 : 5-trideuterobenzene, we shall require a more expanded statement of the selection rules. Of the twenty vibrations which might be concerned, ten are non-degenerate (A), including four which are totally symmetrical (A_1'), whilst ten are degenerate (E). They fall into five symmetry classes, as shown in Table III, which contains their fundamental frequencies in the electronic ground state, as recorded by Herzfeld, Ingold, and Poole (*loc. cit.*).

TABLE III.

Vibration Classes of D_{3h} Benzenes. Fundamental Frequencies of 1 : 3 : 5-*Trideuterobenzene in the Electronic Ground State* (*cm.*$^{-1}$).

Symmetry :		A_1'.		A_2'.	A_2''.	E'.		E''.
(C)	(1)	956	1004	1600	691	593	1407	373
	(2)					1573		
(H)	(1)	2282	3053	920	533	2292	3084	710
	(2)			1230	915	834	1102	947

For vibrations accompanying the $\mathbf{A_{1g}}$—$\mathbf{B_{2u}}$ electronic transition of a D_{3h} benzene, such as 1 : 3 : 5-trideuterobenzene, the general selection rule is that, in either or both of the combining

states, such vibrations may be excited with such quantum numbers that the product of all the involved vibrational wave-functions has either the symmetry E' or the symmetry A_1''. Some consequences of this rule are given in Table IV (which can be derived from Table XIII, *J.*, 1946, 234).

TABLE IV.

Vibrations allowed in Combination with the $\mathbf{A_{1g}}$—$\mathbf{B_{2u}}$ *Transition of a* D_{3h} *Benzene.*

$\psi'_{\text{vib.}} \cdot \psi''_{\text{vib.}}$	E' (perp. bands).	A_1'' (par. bands).
One quantum (either state)	** E'	—
Two quanta (same or different states)	** E', A_1' † E', E' E', A_2' † E'', E'' E'', A_2''	A_2', A_2'' E', E''
One E' and two other quanta (same state or distributed)	** E', A_1', A_1' E', A_2', A_1' * ,, A_2', A_2' ,, E', A_1' * ,, A_2'', A_2'' ,, E', A_2' * ,, E', E' ,, E'', A_2'' * ,, E'', E''	E', E'', A_1' ,, E'', A_2' ,, E', A_2'' ,, E', E''

The indications **, * and † have the significance described in Section 5, except that, naturally, E' must be read for E_g^+ in the explanation there given, and the symmetry symbols of the illustrations have to be changed. The conditions for band intensification by resonance are exactly as stated in Section 5.

(7) *Vibrational Selection Rules for the* $\mathbf{A_{1g}}$—$\mathbf{B_{2u}}$ *Transition of* V_h *Benzenes.*—The two investigated benzenes of this symmetry are 1 : 4-dideuterobenzene and 1 : 2 : 4 : 5-tetradeuterobenzene. The most notable thing about their vibrations, as compared with those of the benzenes already discussed, is the absence of degeneracy: each degenerate vibration of a D_{6h} benzene becomes replaced in either of these compounds by two distinct vibrations, which may not be very different, or may be widely different, but which in either case go into different symmetry classes.

In the V_h benzenes the electronic transition is again forbidden, although, if the system of nuclear charges belonged to the symmetry group $\mathbf{V_h}$, it would be allowed; but for practical purposes the system of charges still possesses the full symmetry $\mathbf{D_{6h}}$. Those vibrations confer spectral activity which have the symmetry of the E_g^+ or B_{1g} class of the group D_{6h} in respect of those symmetry elements which survive in the sub-group V_h. The required symmetry properties are possessed by the V_h symmetry classes A_g, B_{1g}, and B_{2g}. Vibrations of the two former classes may produce pseudo-perpendicular bands: A_g vibrations can give a transition moment parallel to x, and B_{1g} vibrations a moment parallel to y. Vibrations of the B_{2g} class could give pseudo-parallel bands, with a transition moment parallel to z.

There are six fundamental A_g vibrations, five such B_{1g} vibrations, and one such B_{2g} vibration. Thus a large number of vibrations are in principle capable of producing spectral activity. In fact, the near-ultraviolet spectra are mainly dependent on just those two vibrations into which the doubly degenerate E_g^+(C 1) vibration of a D_{6h} benzene splits when the symmetry is reduced to V_h. They are planar, carbon-bending vibrations, both very similar in form and frequency to the vibration E_g^+(C 1) of a D_{6h} benzene. They fall into the A_g and B_{1g} classes, and we call them A_g(C 1) and B_{1g}(C 1). It follows that, in either electronic state, one quantum of the perturbing vibration can be provided in two ways, whilst two quanta may be furnished in three ways. Thus each of the two active origins, A and B, will now be a close doublet, and the bands of the progressions which proceed from these origins will inherit the doublet character. It follows also that the origins C and D, and their progressions, may contain more complicated band groups.

Progressions can in principle be formed by changes of quantum number, unrestricted by symmetry, in any of the totally symmetrical, A_g, vibrations. However, all the more important progressions which in fact appear in the absorption and fluorescence spectra of the V_h benzenes are dependent on symmetry-unrestricted changes in the particular A_g vibration which resembles the ring-swelling, A_{1g}(C), vibration of a D_{6h} benzene. There is only one such vibration, and we call it A_g(C). Thus, apart from the doubling mentioned above, the A and B progressions are on

the whole simpler in the spectra of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene than they are in the spectra of 1 : 3 : 5-trideuterobenzene.

We shall expect negatively-running sequences, due to n—n transitions of vibrations of low frequency, to start from all the stronger bands of the progressions. However, these sequences, while preserving generally the character described for other benzenes, will involve the complication that the responsible vibration, E_u^+(C) of a D_{6h} benzene is degenerate, and becomes split in a V_h benzene into two low-frequency vibrations which we call A_u(C) and B_{1u}(C). The first is identical with one form of the E_u^+(C) vibration, whilst the second is distinct though similar. However, since the two differ quite appreciably in frequency, we must expect that, in place of any one E_u^+(C) sequence of a D_{6h} benzene, sequences in A_u(C) and B_{1u}(C) will both appear, as well, possibly, as mixtures of the two.

The numbers of vibrations contained in each of the eight V_h symmetry classes, and the frequencies which, according to Herzfeld, Ingold, and Poole, they possess in the electronic ground state of 1 : 4-dideuterobenzene and 1 : 2 : 4 : 5-tetradeuterobenzene, are shown in Table V (cf. *J.*, 1946, 272, 288).

TABLE V.

Vibrations of V_h Benzenes and Fundamental Frequencies in the Electronic Ground State (cm.$^{-1}$).

	Symmetry :	A_g.	A_u.	B_{1g}.	B_{1u}.	B_{2g}.	B_{2u}.	B_{3g}.	B_{3u}.
$C_6H_4D_2$	(C)	978	405		367		992	634	1603
	(C 1)	597		601					
	(C 2)	1587		1569			1469		1413
	(H)	1173	970	1309		849	1033		1106
	(H 1)	2280		909	597		2275	736	814
	(H 2)	3055		3042	876		3060	967	3079
$C_6H_2D_4$	(C)	961	352		383		977	615	1585
	(C 1)	589		586					
	(C 2)	1572		1564			1353		1439
	(H)	862	793	954		664	819		812
	(H 1)	3045		1255	548		3078	930	1057
	(H 2)	2285		2272	925		2280	767	2280

The selection rule for vibrations accompanying the $\mathbf{A_{1g}}$—$\mathbf{B_{2u}}$ electronic transition of a V_h benzene is that in either or both of the combining states such vibrations may be excited with such quantum numbers that the product of all the involved vibrational wave-functions has the symmetry A_g, B_{1g}, or B_{2g}. The way in which this rule works out is illustrated in Table VI (cf. Table XIV, *J.*, 1946, 234). The indications ** and * have meanings analogous to those given to the same symbols in the preceding tables. The conditions for band intensification by resonance are as stated in Section 5.

TABLE VI.

Vibrations allowed in Combination with the $\mathbf{A_{1g}}$—$\mathbf{B_{2u}}$ Transition of a V_h Benzene.

$\psi'_{\text{vib.}} \cdot \psi''_{\text{vib.}}$	A_g (x-bands).	B_{1g} (y-bands).	B_{2g} (z-bands).
One quantum (either state)	** A_g	** B_{1g}	—
Two quanta (same or different states)	** A_g, A_g ; * B_{2g}, B_{2g} * A_u, A_u ; * B_{2u}, B_{2u} * B_{1g}, B_{1g} ; * B_{3g}, B_{3g} * B_{1u}, B_{1u} ; * B_{3u}, B_{3u}	** A_g, B_{1g} A_u, B_{1u} B_{2g}, B_{3g} B_{2u}, B_{3u}	A_g, B_{2g} A_u, B_{2u} B_{1g}, B_{3g} B_{1u}, B_{3u}
One A_g, two other quanta (together or dis-tributed)	** A_g, A_g, A_g ; * A_g, B_{2g}, B_{2g} * ,, , A_u, A_u ; * ,, , B_{2u}, B_{2u} ** ,, , B_{1g}, B_{1g} ; * ,, , B_{3g}, B_{3g} * ,, , B_{1u}, B_{1u} ; * ,, , B_{3u}, B_{3u}	** A_g, A_g, B_{1g} ,, , A_u, B_{1u} ,, , B_{2g}, B_{3g} ,, , B_{2u}, B_{3u}	A_g, A_g, B_{2g} ,, , A_u, B_{2u} ,, , B_{1g}, B_{3g} ,, , B_{1u}, B_{3u}
One B_{1g}, two other quanta (together or distributed)	** B_{1g}, A_g, B_{1g} ,, , A_u, B_{1u} ,, , B_{2g}, B_{3g} ,, , B_{2u}, B_{3u}	** B_{1g}, A_g, A_g ; * B_{1g}, B_{2g}, B_{2g} * ,, , A_u, A_u ; * ,, , B_{2u}, B_{2u} ** ,, , B_{1g}, B_{1g} ; * ,, , B_{3g}, B_{3g} * ,, , B_{1u}, B_{1u} ; * ,, , B_{3u}, B_{3u}	B_{1g}, A_g, B_{3g} ,, , A_u, B_{3u} ,, , B_{1g}, B_{2g} ,, , B_{1u}, B_{2u}

It is to be noted that although a B_{2g} vibration is allowed by its symmetry classification to produce a z-band, the one available fundamental vibration of that symmetry class, the vibration B_{2g}(H), can be shown by more detailed considerations to be of no use for that purpose. For the normal co-ordinate of this vibration of a V_h benzene is exactly the same as one normal co-ordinate of an E_g^- vibration of a D_{6h} benzene (Herzfeld, Hobden, Ingold, and Poole, *J.*, **1946**, 285; cf. their diagram XII). Therefore the B_{2g}(H) vibration of a V_h benzene has the symmetry $\mathbf{E_g^-}$ with respect to the symmetry $\mathbf{D_{6h}}$ of the system of nuclear charges; and a perturbation of this symmetry does not produce bands. That is why the top right-hand compartment of Table VI contains a blank, whereas symmetry considerations, without a normal co-ordinate treatment, would have allowed us to insert B_{2g}.

(8) *Vibrational Selection Rules for the* $\mathbf{A_{1g}}$—$\mathbf{B_{2u}}$ *Transition of a* C_{2v} *Benzene.*—Monodeuterobenzene has the symmetry C_{2v}. Its ultraviolet spectra, while generally resembling those of D_{6h} benzenes, may exhibit the additional features of the spectra of the D_{3h} benzene, as well as those of the spectra of the V_h benzenes; for C_{2v} is a sub-group of both D_{3h} and V_h, as well as of D_{6h}.

The electronic transition is still forbidden. There are no degenerate vibrations. Those vibrations confer spectral activity which have the symmetry properties of the E_g^+ or B_{1g} class of the group D_{6h} in respect of those symmetry elements which survive in the sub-group C_{2v}. Such vibrations belong to the C_{2v} symmetry classes A_1, B_1, and A_2; and they are allowed to produce x-bands, y-bands, and z-bands, respectively.

In spite of the large number of allowed vibrations, the ultraviolet band system is again overwhelmingly dependent on perturbations by just those two vibrations into which the doubly degenerate E_g^+(C 1) vibration of D_{6h} benzene splits when the symmetry is degraded to C_{2v}. These two planar, carbon-bending vibrations are closely similar in form and frequency to the E_g^+(C 1) vibration of a D_{6h} benzene. They fall into the symmetry classes A_1 and B_1, and we shall call them A_1(C 1) and B_1(C 1). Thus in the spectra, the active origins A and B should become double, whilst C and D could become multiple, just as described for the V_h benzenes (Section 7).

The selection rules would allow progressions to arise by unrestricted quantum changes in any of the totally symmetrical A_1 vibrations. But in fact, the most important progressions depend on quantum changes in that totally symmetrical vibration, called A_1(C), which most closely resembles the ring-swelling, A_{1g}(C), vibration of a D_{6h} benzene.

We expect negatively-running sequences, due to n—n transitions of low-frequency vibrations, to start from the stronger bands of the main progressions. Corresponding to the degenerate, E_u^+(C), vibration, which, in a D_{6h} benzene, is responsible for such sequences, and to the two responsible vibrations, A_u(C) and B_{1u}(C), of a V_h benzene, there are two, which we call A_2(C) and B_2(C), in a C_{2v} benzene. The first is identical with one form of the E_u^+(C) vibration of a D_{6h} benzene, and with the A_u(C) vibration of a V_h benzene; the second is different from any other vibration. Thus, in place of any particular sequence in a spectrum of a D_{6h} benzene, we may expect overlapping sequences in the vibrations A_2(C) and B_2(C), and also mixed sequences involving both vibrations.

The numbers of vibrations in each of the four C_{2v} symmetry classes, and the frequencies which they possess in the electronic ground state of monodeuterobenzene, according to the determinations of Bailey, Gordon, Hale, Herzfeld, Ingold, and Poole (*J.*, 1946, 299), are shown in Table VII.

TABLE VII.

Vibrations of C_{2v} *Benzenes. Fundamental Frequencies of Monodeuterobenzene in the Electronic Ground State* (*cm.*$^{-1}$).

Symmetry:	A_1.			B_1.		A_2.		B_2.	
(C)	980		1007	1624		405		380	698
(C 1)	601			603					
(C 2)	1591		1480	1574	1450				
(H)	1176		1031	1292	1076	970	850		
(H 1)	2269			1158	858			608	778
(H 2)	3054	3060	3065	3041	3079			992	995

The general selection rule for vibrations accompanying the $\mathbf{A_{1g}}$—$\mathbf{B_{2u}}$ transition of a C_{2v} benzene is that in either or both of the combining states such vibrations may be excited with such quantum numbers that the product of all the involved vibrational wave-functions has the symmetry A_1, B_1, or A_2. The one exception to this is that a single quantum of an A_2 vibration cannot produce spectral activity, because it happens that each of the three fundamental vibrations

of the A_2 class satisfies the further condition of having either $\mathbf{E}_g^-$ or $\mathbf{E}_u^+$ symmetry with respect to the $\mathbf{D}_{6h}$ system of nuclear changes, and either of these conditions is sufficient to cancel the transition moment. These rules are illustrated in Table VIII. The significance of the intensity indications ** and *, and the rules governing intensification by resonance, are as explained for the more symmetrical benzenes.

TABLE VIII.

Vibrations Allowed in Combination with the $\mathbf{A_{1g}}$—$\mathbf{B_{2u}}$ *Transition of a* C_{2v} *Benzene.*

$\psi'_{vib.} \cdot \psi''_{vib.}$	A_1 (*x*-bands).	B_1 (*y*-bands).	A_2 (*z*-bands).
One quantum	** A_1	** B_1	—
Two quanta	** A_1, A_1 * A_2, A_2 * B_1, B_1 * B_2, B_2	** A_1, B_1 A_2, B_2	A_1, A_2 B_1, B_2
One A_1, two other quanta	** A_1, A_1, A_1 * A_1, A_2, A_2 * ,, , B_1, B_1 * ,, , B_2, B_2	** A_1, A_1, B_1 ,, , A_2, B_2	A_1, A_1, A_2 ,, , B_1, B_2
One B_1, two other quanta	** B_1, A_1, B_1 ,, , A_2, B_2	** B_1, A_1, A_1 * B_1, A_2, A_2 * ,, , B_1, B_1 * ,, , B_2, B_2	B_1, A_1, B_2 ,, , A_2, B_1

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96. *Excited States of Benzene. Part II. Analysis of the First Ultraviolet Band System of the Absorption Spectrum of Benzene.*

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The measurements of Radle and Beck on the ultraviolet absorption spectrum of benzene are analysed according to the requirements outlined in the abstract of Part I. A list is given of eleven fundamental frequencies of the upper electronic state. They are all assigned to vibrations, but in this paper the assignments are supported only by evidence which is internal to the spectrum under consideration. An important part of the basis of some of the assignments depends on comparisons between the ultraviolet absorption and fluorescence spectra of different isotopically substituted benzenes. Such arguments of comparison are reserved for collective treatment in Part XI.

(1) *Data.*—An extensive series of measurements on the first ultraviolet absorption system of benzene has been recorded by Radle and Beck (*J. Chem. Physics*, 1940, **8**, 507), who also made a number of assignments. For the continued analysis of the spectrum our procedure was first to select from their list of measured intensity maxima all those which stand out prominently from their background of weak, overlapped bands. It is unlikely that any of these more prominent frequencies represents a branch of some separately listed band; or that any is an accidental intensity maximum caused by overlapping; and, furthermore, all these bands seem strong enough to demand some fairly simple explanation in terms of allowed vibrational changes.

The frequencies and intensities of all the bands which seemed to us worth trying to assign are in Table I. The Table also contains our assignments. Most of the older assignments are adopted, though some have had to be changed; many assignments are new. The result is that none of the frequencies which we originally thought should be explained now remains without a plausible explanation.

The assignments are expressed by means of a literal notation, the key to which is in Tables II and III. The meanings of the subscripts and superscripts are explained in the Note below Table I: they can also be understood from the examples given in Figs. 1 and 2 of Part I. The letters by which the equations of Table II are represented have been chosen to correspond as far as possible to those used previously. Equations A—G (p. 419) agree with those given by Sponer, Nordheim, Sklar, and Teller (*J. Chem. Physics*, 1939, **7**, 207), except for certain dropped or added terms. The ranges of quantum numbers, given on the right in Table II, relate only to the listed, prominent bands: larger ranges could often be given by taking account of bands, which, though definite, do not stand out strongly against their environment.

TABLE I.

Absorption Spectrum of Benzene. Frequencies and Intensities (Radle and Beck); and Assignments (cf. Tables II and III).

Freq. (cm.$^{-1}$).	Inty.	Assgnt.	Freq. (cm.$^{-1}$).	Inty.	Assgnt.	Freq. (cm.$^{-1}$).	Inty.	Assgnt.
36317·2	2	F_0^1, B_{-1}^1	38891·3	25	H_1^0	40202·5	140	C_2^1
334·6	1		919·9	55	G_0^1	248·3	160	B_3^0
478·0	3	F_0^0, B_{-1}^0	929·0	55		252·5	160	
496·2	4		967·0	30	U_0^1	292·8	510	A_2^1
624·7	3	A_{-2}^0	39010·0	25	B_2^2	297·7	350	
990·7	8	B_0^3	038·6	170	Y_0^0	319·8	130	E_1^1
37000·9	8		047·0	25	A_1^3	344·7	160	
156·8	25	B_0^2	056·0	25		366·4	420	C_2^0
160·2	25		063·0	25		372·0	230	
216·7	18	N_0^0	082·0	250	G_0^0	456·0	6500	A_2^0
230·2	21	D_0^1	086·8	250		482·7	335	E_1^0
321·1	140	B_0^1	122·0	25	C_1^2	489·4	325	
392·5	55	D_0^0	124·0	25		543·0	35	O_1^1
452·5	25	A_{-1}^1	134·2	130	U_0^0	558·9	250	K_1^0
457·3	12		168·5	130	B_2^1	686·5	170	O_1^0
481·9	420	B_0^0	204·5	280	A_1^2	704·8	335	
616·8	85	A_{-1}^0	209·3	230		812·2	55	U_2^1
766·8	25	J_0^2	215·6	140		840·1	25	Q_{-2}^2
926·8	35	J_0^1	236·0	150	D_2^0	883·3	30	Y_2^0
956·5	18	H_0^0	255·1	170	M_1^0	894·5	30	R_0^0
962·6	12		265·5	170		903·5	55	
967·8	25		272·1	140		930·4	55	G_2^0
990·8	18	D_1^2	281·4	170	C_1^1	968·5	230	U_2^0
38043·8	30	C_0^3	330·6	350	B_2^0	41002·3	190	Q_{-2}^1
084·1	55	B_1^2	371·2	750	A_1^1	028·5	55	A_3^2
089·4	12		376·1	510		053·9	55	
121·8	25	A_0^3	398·9	130	E_0^1	075·9	120	W_1^0
125·4	18		423·1	160		081·7	120	
133·2	35		445·3	675	C_1^0	099·7	140	M_{-2}^0
141·3	30	N_1^0	487·1	55	I_1^0	165·3	450	Q_{-2}^0
154·0	30	D_1^1	534·2	7000	A_1^0	173·5	55	B_4^0
204·3	55	C_0^2	560·8	335	E_0^0	218·4	350	A_3^1
210·0	55	L_0^0	568·7	250		239·6	75	E_2^1
245·4	160	B_1^1	638·2	335	K_0^0	266·6	140	
281·1	230	A_0^2	765·4	190	O_0^0	285·7	210	C_2^0
285·2	210		783·2	250		377·9	3500	A_3^0
292·3	170		841·5	55	G_1^1	399·2	170	E_2^0
316·6	130	D_1^0	847·3	45		402·3	170	
343·3	190	M_0^0	850·7	70		409·9	190	
350·0	140		894·1	55	U_1^1	478·6	350	K_2^0
359·7	250	C_0^1	962·1	120	Y_1^0	606·6	140	O_2^0
365·2	160		971·9	70	A_2^2	624·3	325	
407·0	550	B_1^0	40004·8	140	G_1^0	700·1	55	T_0^0
448·4	950	A_0^1	010·2	160		741·0	140	S_0^0
452·4	950		023·6	40	X_0^0	760·9	70	Q_1^2
523·0	630	C_0^0	050·2	190	U_1^0	824·1	25	R_1^0
562·4	140	I_0^0	090·8	55	B_3^1	884·5	160	U^0
612·2	7500	A_0^0	109·1	85	A_2^2	923·9	160	Q_1^1
649·0	25	P_0^0	131·5	230		974·1	140	Z_0^0
655·0	25		137·3	55		42018·9	55	M_4^0
766·9	21	G_0^2	159·9	210	W_0^0	088·0	100	Q_1^0
839·7	35	J_1^1	177·7	230	M_2^v	111·8	70	
851·5	35		186·8	140		137·6	85	A_4^1

TABLE I—*contd.*

Freq. (cm.$^{-1}$).	Inty.	Assgnt.	Freq. (cm.$^{-1}$).	Inty.	Assgnt.	Freq. (cm.$^{-1}$).	Inty.	Assgnt.
42204·1	55	C_4^0	42845·0	130	Q_2^1	43929·1	160	Q_3^0
286·6	250	A_4^0	892·1	40	Z_1^0	952·9	40	
297·7	950		43009·3	325	Q_2^0	44133·0	35	A_6^0
318·3	160	E_3^0	032·0	85		488·8	30	S_3^0
328·2	40		215·8	300	A_5^0	847·9	35	Q_4^0
396·9	55	K_3^0	573·7	170	S_2^0	869·8	25	
544·2	110	O_3^0	716·6	35	U_6^0	45050·4	18	A_7^0
621·1	55	T_1^0	765·6	25	Q_3^1	402·9	13	S_4^0
658·2	140	S_1^0	808·9	25	Z_2^0	766·1	12	Q_5^0
800·9	130	U_4^0				786·5	9	

Note: In the assignment columns the upper-state quantum number, denoted by p' in Table II, is given as a simple subscript, and the lower-state quantum number, p'', as a subscript with a negative sign; these mark progressions in A_{1g}(C). The quantum number s of Table II, which is common to both states, is given in the assignment columns as a superscript; it marks sequences in E_u^+(C).

As is apparent from Table I a close group of intensity maxima is often regarded as a single band. Which maxima should be so grouped is a matter for judgment, the main guide being the appearance of the spectrum. Presumably owing to the rotational structure, many bands are double headed; and some bands contain one or more additional maxima. Apart altogether from rotation, certain vibrational effects are expected to lead to complexity of band structure. One possible cause of this kind is the near-superposition of bands which involve 0—0 and 1—1 transitions with respect to some vibration whose frequency is nearly the same in the upper and lower electronic states: benzene has at least one such frequency. Another cause is the splitting, due to the anharmonicity of the vibrations, of those higher-order degeneracies which would otherwise characterise overtones and combinations of degenerate fundamental vibrations. Thus the second quantum level of an E_u^+ vibration consists of three close-lying levels, the symmetries of the components being $(E_u^+)^2 = A_{1g}, A_{2g}, E_g^+$ (cf. Table XII, *J.*, 1946, 234). We explain in this way the fact, which may not be particularly conspicuous in tables, but is very obvious in original plates or in microphotometer records made from them, that, as we pass, *e.g.*, along any sequence, 0—0, 1—1, 2—2 . . . , with respect to the vibration E_u^+(C), the complexity of the bands increases notably.

TABLE II.

Absorption Spectrum of Benzene. Key to Series Assignments in Table I.

	Freq. (cm.$^{-1}$).	p'.	p''.	s.
A	= 38090 + 521 + 923p' − 992p'' − 161s	0—7	0—2	0—3
B	= ,, − 608 + 923p' − 992p'' − 161s	0—4	0, 1	0—3
C	= ,, + 2 × 521 − 608 + 923p' − 161s	0—4		0—3
D	= ,, + 521 − 2 × 608 + 923p' − 161s	0—2		0, 1
E	= ,, + 1470 + 923p' − 161s	0—3		0, 1
F	= ,, − 1600 − 161s			0, 1
G	= ,, + 521 + 2 × 243 + 923p' − 161s	0—2		0—2
H	= ,, − 608 + 2 × 243 + 923p'	0, 1		
I	= ,, + 2 × 243 + 923p'	0, 1		
J	= ,, + 923p' − 161s	0, 1		1, 2
K	= ,, + 521 + 2 × 513 + 923p'	0—3		
L	= ,, − 608 + 2 × 365			
M	= ,, + 521 − 265 + 923p'	0—4		
N	= ,, − 608 − 265 + 923p'	0, 1		
O	= ,, + 521 + 2 × 585 + 923p' − 161s	0—3		0, 1
P	= ,, − 608 + 2 × 585 + 923p'			
Q	= ,, + 3080 + 923p' − 161s	0—5		0—2
R	= ,, + 3080 − 265 + 923p'	0, 1		
S	= ,, + 521 + 3130 + 923p'	0—4		
T	= ,, {+ 521 + 3080 + 923p' / + 2 × 243 + 3130 + 923p'}	0, 1		
U	= ,, + 2 × 521 + 923p' − 161s	0—5		0, 1
W	= ,, + 521 + 2 × 775 + 923p'	0, 1		
X	= ,, + 521 + 2 × 706			
Y	= ,, {+ 365 + 585 + 923p' / + 243 + 706 + 923p'}	0—2		
Z	= ,, + 3885 + 923p'	0—2		

Note: The frequency 38090 cm.$^{-1}$ is that of the electronic origin. The other frequencies are vibration frequencies: they are assigned to vibrations in Table III. Concerning the frequency 3885 cm.$^{-1}$, see text (Section 8).

TABLE III.

Absorption Spectrum of Benzene. Assignment to Vibrations of the Vibration Frequencies (cm.$^{-1}$) contained in Table II.

Upper-state fundamental frequencies (+).	Lower-state fundamental frequencies (−).	Diffs. of upper- and lower-state fundamentals (−).	Vibration.
923	992	69	A_{1g}(C)
3130	—	—	A_{1g}(H)
513	—	—	A_{2u}(H)
365	—	—	B_{2g}(C)
775	—	—	B_{2g}(H)
521	608	87	E_g^+(C 1)
1470	1600	—	E_g^+(C 2)
3080	—	—	E_g^+(H 1)
243	—	161	E_u^+(C)
706	—	—	E_u^+(H)
585	—	265	E_g^-(H)

(2) *Band Series* A, B, C *and* D.—As explained in Part I, Section 4, these bands determine he general pattern of the spectrum. Three vibrations are involved, *viz.*, E_g^+(C 1), unit quantum changes in which create the four spectrally active origins, A_{1g}(C), multiple quantum changes in which give the progressions, and E_u^+(C), which by null quantum changes produces the sequences.

The active origins determine the forbidden electronic origin,

$$J_0^0 = 38090 \pm 2 \text{ cm.}^{-1}$$

whilst the bands collectively give the following fundamental frequencies,

$$E_g^+(\text{C 1})_{\text{ground}} = 608 \text{ cm.}^{-1} \qquad E_g^+(\text{C 1})_{\text{excited}} = 521 \text{ cm.}^{-1}$$
$$A_{1g}(\text{C})_{\text{ground}} = 992 \text{ cm.}^{-1} \qquad A_{1g}(\text{C})_{\text{excited}} = 923 \text{ cm.}^{-1}$$

as well as the frequency difference,

$$E_u^+(\text{C})_{\text{ground}} - E_u^+(\text{C})_{\text{excited}} = 161 \text{ cm.}^{-1}$$

The long progressions of series A, B and C show the effect of anharmonicity in the ring-breathing vibration of the upper electronic state. The frequency drops from an average initial value of 923·5 cm.$^{-1}$ for the first full quantum to 917 cm.$^{-1}$ for the seventh. Apart from a casual scatter of ± 1 cm.$^{-1}$ the fall is linear. It seems to make only a very small difference whether, in the upper electronic state, the stack of A_{1g}(C) levels rises from the zero-point level (as for series B), or is superposed on one quantum of the E_g^+(C 1) vibration (series A), or on two such quanta (series C). The linear frequency fall indicates an energy formula of the usual anharmonic type,

$$E/h = \nu(p' + 1/2) - x\nu(p' + 1/2)^2,$$

with $\nu = 924$ cm.$^{-1}$ and $x\nu = 0{\cdot}5$ cm.$^{-1}$.

(3) *Band Series* E *and* F.—A unit quantum change in any of the four E_g^+ vibrations, superposed on the A_{1g}—B_{2u} electronic change, can in principle produce a non-vanishing transition moment; and the origin E_0^0 of the positive E progression in 923 cm.$^{-1}$, and of the related negative sequences in 161 cm.$^{-1}$, has been assumed by Sponer, Nordheim, Sklar, and Teller (*loc. cit.*) to arise in consequence of an upward 0—1 transition of the carbon-stretching vibration, E_g^+(C 2).

In the electronic ground state, this vibration is well known from the Raman spectrum of liquid benzene: unperturbed, its frequency as given in this spectrum would be about 1596 cm.$^{-1}$; but it becomes mixed with the combination E_g^+(C 1)606 + A_{1g}(C) 992 = 1598 cm.$^{-1}$, and the frequencies resulting from the resonance are found at 1585 and 1606 cm.$^{-1}$. The frequency of the vibration in the electronically excited state, as given by the position of the E_0^0 band in the absorption spectrum of benzene vapour, would be approximately 1470 cm.$^{-1}$. Sponer has, however, drawn attention to the difficulty that the corresponding band of hexadeuterobenzene is somewhat displaced from the position in which we should expect it, if the plausible assumption be made that the ratio of the E_g^+(C 2) frequencies in the upper and lower electronic states should be nearly the same in benzene and hexadeuterobenzene. In consequence, she considered, but

did not actually recommend, alternative assignments for the E bands (*J. Chem. Physics*, 1940, **8**, 705). Having examined the absorption spectra of a number of deuterated benzenes, we confirm Sponer's observation as part of a general phenomenon : all the absorption spectra possess prominent " E " series of bands, but the positions of the E_0^0 origins are appreciably irregular.

Our study of the fluorescence spectra of various deuterated benzenes has disclosed another apparent anomaly. Corresponding to the E bands of the absorption spectrum, we should expect, in fluorescence, a prominent progression of bands having an origin, F_0^0, related to B_0^0, the main active origin for fluorescence, just as E_0^0 is related to A_0^0, the main active origin for absorption. The origin F_0^0 would lie below the electronic origin, J_0^0, by a frequency interval equal to the ground-state frequency of the E_g^+(C 2), or E_g^+(C 2)-like, fundamental vibration—a frequency which for benzene and all deuterated benzenes is known from Raman spectra. However, in our experience, an F progression is never prominent in fluorescence, save in such a case as that of benzene itself, in which there is a special reason for a strong appearance. This reason is that the B and F progressions become of necessity mixed together by the already-mentioned resonance arising in the ground state of benzene from the near-degeneracy of the E_g^+(C 2) fundamental frequency with the E_g^+(C 1) + A_{1g}(C) combination tone. This resonance allows the E_g^+(C 2) fundamental vibration to " borrow " spectral activity from the highly active combination E_g^+(C 1) + A_{1g}(C), just as, conversely, in the Raman effect, the intrinsically weak combination " borrows " activity from the strong fundamental—the transfer of intensity being in each case associated with displacements of frequency.

In spite of these two difficulties, we believe that the original assignment of Sponer, Nordheim, Sklar, and Teller is correct. We assume a resonance quite analogous to that just mentioned, but in the electronically excited state. In particular, we assume that the E bands, although allowed by symmetry under this assignment, would not in fact be strong enough for observation (at least under our conditions) in the absorption spectrum of any benzene, were they not able to " borrow " most of their intensity from the closely neighbouring A bands. The associated frequency shifts, mostly borne by the E bands because of their relative weakness, account, according to our picture, for the somewhat displaced positions in which we find certain of the E_0^0 origins. Typically, the assumed resonance is between the strongly active combination tone, E_g^+(C 1) + A_{1g}(C), and the weakly active fundamental frequency, E_g^+(C 2), both of the upper electronic state. In all the benzenes we have studied, these frequencies, as determined by the position of the A and E bands, that is, after any separation caused by resonance, lie 1—3% apart, the fundamental giving the E bands having always a higher frequency than the combination which produces the A bands. Now Herzfeld, Ingold, and Poole (*J.*, 1946, 327) surveyed all the known cases of resonance, due to accidental degeneracy between fundamentals and combination tones of identical symmetry, in the electronic ground states of benzenes : their data were in the Raman and infra-red spectra of ordinary benzene and several of its deuterated derivatives. They found marked intensification of the weaker of the interacting frequencies to be usual when, after any displacement resulting from resonance, the frequencies lay 2—4% apart. They also found that frequencies which, apart from their resonance, would have lain within 1% of each other, usually underwent a further separation of the order of 1%. Thus our postulated resonance effects of the electronically excited state seem plausible, and indeed, typical. We may assume that in benzene, for example, the relevant frequencies would, apart from their resonance, fall rather more closely together than in, say, hexadeuterobenzene, with the result that the frequency controlling the position of the E_0^0 origin will be raised by resonance somewhat more in the former case than in the latter.

The strength of the resonance effects arising from an accidental near-degeneracy of a fundamental frequency with a combination tone of the same symmetry class depends, not only on the frequency separation, but also on the force system. In the force system characterising the electronic ground state of benzene, marked resonance effects in general arise, as we have seen, when the nearly degenerate, unperturbed frequencies lie up to 4% apart. We also know, however, that, in the ground state of benzene, the particular resonance in which we are now interested, *viz.*, that between the E_g^+(C 2) fundamental and the E_g^+(C 1) + A_{1g}(C) combination, is not quite typical in this respect. In fact, this case of resonance is more restricted than many, since, for a given separation of the unperturbed frequencies, smaller effects are observed than appear in analogous cases. For evidence we again turn to Raman spectra. It is true that with benzenes in which the unperturbed frequencies E_g^+(C 2) and E_g^+(C 1) + A_{1g}(C) of the ground state are practically coincident, large resonance effects are found in the Raman spectrum. But with hexadeuterobenzene, and also with 1 : 3 : 5-trideuterobenzene, in each of which the relevant frequencies lie 2% apart, no marked resonance effects involving these frequencies are

observed. We restrict illustration to these cases, because, in other benzenes, each of the E_g^+-like fundamental frequencies itself splits into two, and this introduces a complication. Now, corresponding to our hypothesis concerning absorption, *viz.*, that the perturbation produced by an E_g^+(C 2) fundamental vibration of the upper electronic state would not generate E bands strong enough for our observation, unless they could " borrow " intensity from neighbouring A bands, we assume that, in fluorescence, an E_g^+(C 2) fundamental of the ground state would not give prominent F bands, unless they could analogously " borrow " intensity from neighbouring B bands. Whether they can thus borrow intensity depends on that amount of mixing of the wave functions, which, when symmetry permits, and the frequencies are close enough to present no great obstacle, is in fact engendered by the force system. But the amount of mixing is already indicated by the " borrowings " observed in Raman spectra : they arise from the same " mixings ", even though the intensity transferences are in the opposite direction. Thus we can partly understand, by reference to the Raman spectra, how in fluorescence an F series of bands is observed with benzene, but not with 1 : 3 : 5-trideuterobenzene or hexadeuterobenzene.

Two F bands are observed in the absorption spectrum of benzene, but they are naturally very weak. They involve upward 1—0 transitions, and, because of the high frequency of the E_g^+(C 2) vibration in the electronic ground state, they are greatly weakened by the small Boltzmann factor of the initial vibrational level.

The E bands have a double-band structure, the maximum at the lower frequency being the stronger. We accept this frequency as being the best available approximation to the vibrational origin. The resonance splitting involving the F bands is nearly symmetrical. Therefore we take the mean of the split maxima as giving the fundamental frequency of the unperturbed vibration. The result of this assumption is in qualitative accord with the intensities of the split bands.

The fuller study of the F series which is possible with the aid of the fluorescence spectrum is described in Part III, Section 2. Taking account of both the absorption and fluorescence spectra, we derive the following fundamental frequencies :

$$E_g^+(\mathrm{C}\ 2)_{\mathrm{ground}} = 1600\ \mathrm{cm.^{-1}} \quad E_g^+(\mathrm{C}\ 2)_{\mathrm{excited}} = 1470\ \mathrm{cm.^{-1}}$$

The value for the ground state, as given by the Raman spectrum of liquid benzene, is 1596 cm.$^{-1}$.

(4) *Band Series* G, H, I, *and* J.—The three positive progressions in 923 cm.$^{-1}$, labelled G, H, and I, start at a common distance of approximately 480 cm.$^{-1}$ above the active origins A_0^0 and B_0^0, and the forbidden electronic origin J_0^0, respectively. The common separation can be shown to represent the first overtone of the out-of-plane vibration E_u^+(C) of the excited state (see below). As noted in Section 1, the two-quantum level of this degenerate vibration is triple, with the associated symmetries A_{1g}, A_{2g} and E_g^+. The symmetry principles outlined in Part I, Section 5, show that transitions from the " vibrationless " level of the electronic ground state can end only on an E_g^+ level. Therefore only the E_g^+ form of the overtone can be involved in the transition giving the first band I_0^0 of the progression which starts about 480 cm.$^{-1}$ above the electronic origin J_0^0. The same symmetry principles (*loc. cit.*) show that transitions which start from the first E_g^+(C 1) vibrational level of the ground electronic state may terminate on any of the three overtone levels, but are expected to end predominantly on the A_{1g} level. Therefore this level chiefly, and the others to a smaller extent, may be involved in the transition giving the first band H_0^0 of the progression which starts about 480 cm.$^{-1}$ above B_0^0. Transitions from the vibrationless ground state can also end on any of the complex group of higher levels which are obtained by combining each of the three forms of the E_u^+(C) overtone of the upper electronic state with the E_g^+(C 1) fundamental frequency of the upper state. Such transitions can combine to produce the initial band G_0^0 of the progression which starts about 480 cm.$^{-1}$ above A_0^0.

Actually, the first band of the I progression appears to be simple in structure : its separation from J_0^0 is 473 cm.$^{-1}$. This we take to be the frequency of the E_g^+ form of the E_u^+(C) overtone. The first band of the H progression is triple : the separations of the components from B_0^0 are 486, 481 and 474 cm.$^{-1}$. Since the first of these components is the strongest, one is tempted to associate it with the A_{1g} form of the overtone; the second and third components might then be related to the A_{2g} and E_g^+ forms, respectively. The first band of the G progression has two main components, as well as several minor components grouped about them; and the separations of the major components from A_0^0 are 475 and 470 cm.$^{-1}$. This is a complicated case, and all that can be suggested is that the generally smaller separations may be connected with the greater effects of anharmonicity in the higher vibrational combinations of the excited state which are concerned in these transitions. Associated with the stronger bands of the G progression one finds sequences in the interval 161 cm.$^{-1}$. These evidently represent 0—2, 1—3, 2—4 . . .

transitions of the E_u^+(C) vibrations—transitions which are allowed by the selection rules to appear with low intensity (cf. Part I, Section 5).

In addition to the many negative sequences in 161 cm.$^{-1}$, already mentioned or to be later discussed, there is one special one, which starts as if from the electronic origin, except that the band in this position is missing. The first actual band, 161 cm.$^{-1}$ lower, is also the starting point of a positive progression in 923 cm.$^{-1}$. Collectively these bands form series J. Sponer, Nordheim, Sklar, and Teller have already explained them. The explanation is closely analogous to that given above to the I bands, which start with a first overtone of the E_u^+ vibration superposed on the electronic origin, and appear because one of the states containing two quanta of the vibration E_u^+(C) has the symmetry E_g^+. The presence of one quantum of an E_u^+(C) vibration in both the lower and upper electronic states will fulfil the same symmetry conditions as if both quanta were present in the upper state, or both in the lower state (cf. Part I, Section 5).

We take the largest value, 486 cm.$^{-1}$, of the upper-state overtone frequency as likely to be the least disturbed by anharmonicity. This figure, and the well-established sequence interval 161 cm.$^{-1}$, representing the difference between the fundamental frequencies in the lower and upper electronic states, leads to the following fundamental frequencies

$$E_u^+(\mathrm{C})_{\mathrm{ground}} = 404 \text{ cm.}^{-1} \quad E_u^+(\mathrm{C})_{\mathrm{excited}} = 243 \text{ cm.}^{-1}$$

An argument leading to the adopted assignment can be based on the existence of series I and J: their direct association with the forbidden electronic origin shows the vibration to be degenerate (cf. Part I, Section 5). Therefore it has to belong to the symmetry class E_u^+, since all other degenerate vibrations are allowed either in the infra-red or the Raman spectrum, and are therefore very well known. There is a carbon and a hydrogen vibration of the E_u^+ class, and the low values of the frequencies show that they can only belong to the carbon vibration E_u^+(C). Confirmation follows from the actual value of the ground-state frequency. The vibration, though forbidden in the Raman effect, actually appears very weakly in the Raman spectrum of liquid benzene owing to the perturbing effect of liquid forces; and partly on this evidence, and partly from a study of Raman and infra-red combination tones, Herzfeld, Ingold, and Poole gave the ground-state frequency of the vibration as 405 cm.$^{-1}$ (*loc. cit.*), in close agreement with the value now determined. Further confirmation comes from the fluorescence spectrum (Part III, Section 3). All the evidence confirms the conclusions of Kistiakowsky and Solomon, already summarised in Part I, Section 4.

(5) *Band Series* K *and* L.—We deal here with some bands believed to depend on two other vibrations having a connexion with the sequence interval 161 cm.$^{-1}$. A band K_0^0 of moderate strength, the starting point of a progression K, lies at 1026 cm.$^{-1}$ above A_0^0. The intensity of the band suggests that the excitation of some quite simply constituted harmonic of the upper electronic state is superposed on the electronic and vibrational transition characteristic of the main active origin A_0^0. It would be natural to try to confirm this assumption by looking for a considerably weaker band 1026 cm.$^{-1}$ above B_0^0: such a band would, however, be obscured by the strong band C_0^0. We may also look for a band, again much weaker than K_0^0, 1026 cm.$^{-1}$ above C_0^0: here we find a band of about the right intensity (at 39522·2 cm.$^{-1}$; intensity 55): it is omitted from Table I only because, lying amongst rather strong bands, it was not originally selected as prominent enough to demand a simple explanation. A corresponding band 1026 cm.$^{-1}$ above D_0^0 would be too weak for observation.

We assign the frequency 1026 cm.$^{-1}$, which by the selection rules must correspond to total symmetry (cf. Part I, Section 5), as the first-overtone frequency in the upper electronic state of the out-of-plane, hexagonal, hydrogen vibration, A_{2u}(H). The reasons for the assignment will be given in Part XI: they depend largely on comparisons among different isotopically modified benzenes. The difference between the fundamental frequencies of the A_{2u}(H) vibration in the upper and lower electronic states is practically the same as the corresponding difference, 161 cm.$^{-1}$, for the E_u^+(C) vibration. It is therefore probable that the 1—1 transitions of the A_{2u}(H) vibration contribute part of the intensity of the 1—1 bands of all those sequences in 161 cm.$^{-1}$ which start from bands of the A and B progressions: the A_{2u}(H) transitions should not contribute to series J, which depends fundamentally on the degenerate nature of the E_u^+(C) vibration (cf. Part I, Section 5). In the absorption spectrum of hexadeuterobenzene (Part IV), for which molecule the E_u^+(C) and A_{2u}^+(H) sequence intervals no longer coincide, we see the 1—1 bands of the A_{2u}(H) vibration separately in the sequences belonging to the A and B progressions.

A well-marked band L_0^0 of rather low intensity lies 120 cm.$^{-1}$ above the electronic origin. It is difficult to explain on the basis of a loss of lower-state quanta in transitions terminating as do those of A_0^0 or C_0^0. We therefore interpret it as representing a gain of upper-state quanta

superposed on the electronic and vibrational transitions of B_0^0 : a similar relationship with D_0^0 is improbable on grounds of intensity. On this basis the upper-state vibration frequency is 730 cm.$^{-1}$, and must correspond to a harmonic of total symmetry (Part I, Section 5). We assign it in what seems to be the only possible way, *viz.*, as the first overtone of the smallest fundamental frequency but one, that of the trigonal, out-of-plane, vibration, B_{2g}(C). The same fundamental frequency appears (Section 8) in the interpretations of another progression (Y). The assignment of the frequency to the B_{2g}(C) vibration is supported by comparisons with other spectra, and by calculations based on a simplified potential system (Part XI).

The B_{2g}(C) vibration is one that could produce n—n sequences, of which at least the 1—1 bands might possess an appreciable intensity. However, the 1—1 bands would be over-lapped by the 2—2 bands of the strong E_u^+(C) sequences, and, as has been explained (Section 1), these bands are broad and multiple. Although we are not able to identify the 1—1 bands of the B_{2g}(C) vibration in the complex contours of the 2—2 bands of E_u^+(C) sequences, the B_{2g}(C) vibration may contribute appreciably to the total intensity of such bands. For in the absorption spectrum of hexadeuterobenzene (Part IV), each 2—2 band of the E_u^+(C) sequences contains a maximum well removed from the head, and so distinctive in appearance that we assign it as the 1—1 band of the B_{2g}(C) vibration.

Two fundamental frequencies of the upper electronic state of benzene follow from our assignment of the bands discussed :

$$A_{2u}(\mathrm{H})_{\mathrm{excited}} = 513 \text{ cm.}^{-1} \quad B_{2g}(\mathrm{C})_{\mathrm{excited}} = 364 \text{ cm.}^{-1}$$

(6) *Band Series* M, N, O, *and* P.—Sponer has already drawn attention (*loc. cit.*) to bands in the absorption spectrum of benzene which lie 265 cm.$^{-1}$ below the active origins A_0^0 and B_0^0, and below the electronic origin J_0^0. A weak band in the last-named position certainly exists (37822·8 cm.$^{-1}$; intensity 9), though we did not think it prominent enough to include in Table I. However, the bands M_0^0 and N_0^0, 265 cm.$^{-1}$ below A_0^0 and B_0^0 respectively, are prominent, and both start positive progressions in 923 cm.$^{-1}$. Band M_0^0 is the stronger, the intensity ratio of M_0^0 to N_0^0 being roughly the same as that of A_0^0 to B_0^0. The same two bands M_0^0 and N_0^0 are prominent in the fluorescence spectrum of benzene (Part III, Section 4), although here N_0^0 is the stronger, just as B_0^0 is stronger than A_0^0; and the progressions which they start are now negative in 992 cm.$^{-1}$. In fluorescence we again find a band 265 cm.$^{-1}$ below the electronic origin J_0^0.

These relationships prove that (as Sponer has already suggested) the bands arise from 1—1 transitions in some vibration superposed on the transitions characteristic of A_0^0, B_0^0, or J_0^0, the interval 265 cm.$^{-1}$ being the difference between the frequencies of the vibration in the lower and upper electronic states. The presence of bands associated with J_0^0 shows that the vibration is degenerate (Part I, Section 5). Partly on the internal evidence of these spectra, and partly by comparisons with the spectra of other benzenes, we identify the vibration as the out-of-plane, hydrogen vibration E_g^-(H) (cf. Part XI). It is not excluded that a minor proportion of the intensities of the M and N bands derives from another out-of-plane, hydrogen vibration, E_u^+(H), which happens to have almost the same sequence interval.

The bands O_0^0 and P_0^0 in the absorption spectrum of benzene lie 1170 cm.$^{-1}$ above A_0^0 and B_0^0 respectively. Their intensities are roughly in proportion to those of A_0^0 and B_0^0. They start positive progressions in 923 cm.$^{-1}$, though all but the first member of the weaker P progression fall among stronger bands and were therefore not included in Tables I and II. Some members of the stronger O progression can be seen to be the starting points of sequences in 161 cm.$^{-1}$. The bands of both series are double, but those of the O series are broader and exhibit subsidiary maxima.

These bands clearly involve the excitation in the upper electronic state of some higher harmonic of total symmetry (Part I, Section 5), in combination with the electronic and vibrational transitions characteristic of A_0^0 or B_0^0. For reasons given in Part XI, we identify the higher harmonic frequency, 1170 cm.$^{-1}$, as the first overtone of the vibration E_g^-(H). The greater complexity of the O bands than of the P bands is consistent with an assignment to a degenerate vibration; for the upper states of the O transitions will then contain three degenerate quanta, and will split up into a more complex set of levels than will the upper state of the P transitions, which will contain only two.

From the upper-state overtone frequency, 1170 cm.$^{-1}$, and the sequence interval,* 265 cm.$^{-1}$,

* We consider the main part of the intensity of series M and N to be due to 1—1 transitions of the vibration E_g^-(H) rather than of the vibration E_u^+(H), partly because the Boltzmann factor of the former vibration is larger, and partly because in all these spectra one notices a general correlation of transition probabilities between overtone series and sequences, and the overtone series, O and P, of the vibration E^-(H) are much stronger than is the overtone series X of the vibration E_u^+(H).

supplemented by the observation of a lower-state overtone frequency, 1695 cm.$^{-1}$, in the fluorescence spectrum of benzene (Part III, Section 4), we deduce the following fundamental frequencies of the vibration concerned :

$$E_g^-(\mathrm{H})_{\mathrm{ground}} = 849 \text{ cm.}^{-1} \qquad E_g^-(\mathrm{H})_{\mathrm{excited}} = 585 \text{ cm.}^{-1}$$

The ground-state frequency, as observed in the Raman spectrum of liquid benzene, is 848·9 cm.$^{-1}$.

(7) *Band Series* Q, R, S, *and* T.—We turn to some band series dependent on high vibrational frequencies, due, as we think, to hydrogen-stretching vibrations of the electronically excited molecule. Sponer, Nordheim, Sklar, and Teller sought to determine the values of these hydrogen-stretching frequencies (*loc. cit.*). They directed attention to two bands, one about 2560 cm.$^{-1}$ above B_0^0, and the other about the same distance above A_0^0, each the starting point of a positive progression in 923 cm.$^{-1}$. They suggested that the interval 2560 cm.$^{-1}$ might correspond to the totally symmetrical hydrogen-stretching frequency, A_{1g}(H), in the upper electronic state. The frequency of this vibration in the electronic ground state of benzene, as observed in the Raman spectrum of liquid benzene, is 3062 cm.$^{-1}$.

We propose certain modifications of these assignments for the following reasons. The band 2560 cm.$^{-1}$ above B_0^0 appears to be too strong to be related in the suggested way to the band at about the same distance from A_0^0; and besides, an alternative reading of the spectrum is possible which would make the band 2560 cm.$^{-1}$ above B_0^0 the second, not the first, member of the progression in 923 cm.$^{-1}$ to which it belongs. If we should change the assignment of this band, but try to retain that of the band 2560 cm.$^{-1}$ above A_0^0, then we should have to expect a similar band 1925 cm.$^{-1}$ above the A_0^0 band of the absorption spectrum of hexadeuterobenzene, this position being fixed rather exactly by an application of the product theorem of Teller and Redlich to the A_{1g} vibrations of the upper electronic states of these two benzenes. But Sponer, who examined the absorption spectrum of hexadeuterobenzene, did not find a band near this position. The nearest bands she could observe lay 1821, 1841, and 1873 cm.$^{-1}$ above A_0^0; and of these, the last two were very weak, only the first having an intensity comparable to that of the benzene band. Actually all three bands, on the score of their frequencies, are unacceptable for correlation on the suggested basis with the benzene band. And if we should suppose that, because of some experimental limitation, the expected band, 1925 cm.$^{-1}$ above A_0^0 in the spectrum of hexadeuterobenzene, evaded observation, then there is still a difficulty. For it can be shown that, if the frequency of the A_{1g}(H) vibration of benzene, and therefore the frequencies of each of the six hydrogen-stretching vibrational degrees of freedom of that molecule, should drop, as is suggested, by about 500 cm.$^{-1}$ when the electronic system passes from the ground state into the excited state, then the electronic origin J_0^0, the exact position of which depends on the difference between the vibrational zero-point energies of the ground and excited states, should suffer a much greater shift than is observed when benzene is deuterated to give hexadeuterobenzene. The zero-point energy differences of the hydrogen-stretching frequencies alone would contribute an upward shift of 390 cm.$^{-1}$, whereas the observed upward shift, containing the total effect of all the 30 vibrational degrees of freedom, is only 200 cm.$^{-1}$. Certainly negative (*i.e.*, downward) contributions to the shift are possible, but it is hardly to be believed that the remaining 24 degrees of freedom, many of whose frequencies we know, can collectively contribute a negative shift as large as 190 cm.$^{-1}$.

The strongest of all the high-frequency bands in the absorption spectrum of benzene is the one lying 2560 cm.$^{-1}$ above A_0^0 : we call it Q_0^0. It is the parent of a long progression in 923 cm.$^{-1}$ the bands of which start sequences in 161 cm.$^{-1}$. We assume these bands to involve the excitation of a hydrogen-stretching vibration of the upper electronic state, but we take this vibration to be, not A_{1g}(H), but E_g^+(H 1). Thus, Q_0^0 is ascribed to a transition from the " vibrationless " ground state to the first quantum level of this vibration in the excited state. The band Q_0^0 is regarded as an active origin, comparable to A_0^0 or E_0^0. The vibration responsible for its appearance, E_g^+(H 1), would be expected to produce an appreciable spectral activity, because it deforms the carbon ring, and therefore the potential field of the unsaturation electrons, qualitatively in the same way as, though quantitatively to a smaller extent than, the E_g^+(C 1) vibration, which produces the very strong origin A_0^0 (cf. Fig. 1, *J.*, 1946, 231).

The frequency of the E_g^+(H 1) vibration in the excited state, as given by the separation of Q_0^0 from the electronic origin J_0^0, is 3080 cm.$^{-1}$. The frequency of the same vibration in the ground state, as given in the Raman spectrum, is 3047 cm.$^{-1}$. Thus our assignment leads to the assumption of a small increase in this hydrogen-stretching frequency—and presumably in all hydrogen-stretching frequencies—when the molecule passes from the ground to the excited state. We confirm this below in relation to the totally symmetrical hydrogen-stretching

frequency. The position predicted on the new basis for the band corresponding to Q_0^0 in the absorption spectrum of hexadeuterobenzene agrees well with that of the band which Sponer found 1821 cm.$^{-1}$ above A_0^0, that is, 2320 cm.$^{-1}$ above J_0^0, and would have liked to correlate with the benzene band.

It is convenient to deal next with the two bands of progression R. They are weak bands lying 265 cm.$^{-1}$ below the first two bands of progression Q. Since in our interpretation Q_0^0 is an active origin, analogous to A_0^0, it would be natural to find associated with it the stronger of those sequences, due to n—n transitions, which appear in connexion with A_0^0. The strongest of such sequences, the E_u^+(C) sequence in 161 cm.$^{-1}$, certainly appears, as we have seen. The other two, of which only the 1—1 bands can be observed in connexion with the A series, are the E_g^+(C 1) sequence in 87 cm.$^{-1}$, and the E_g^-(H) sequence in 265 cm.$^{-1}$. The presence, in association with bands of the Q series, of 1—1 bands of sequences in 87 cm.$^{-1}$ cannot be verified because of overlapping. However, along with the two strongest Q bands, 1—1 bands in the other sequence, that in 265 cm.$^{-1}$, clearly appear with about the expected intensity.

We refer next to the progression labelled S, the first member of which, S_0^0, lies 3130 cm.$^{-1}$ above A_0^0. In explanation we assume that an excitation of one quantum of the totally symmetrical hydrogen-stretching vibration, A_{1g}(H), is superposed on the electronic and vibrational changes that produce the active origin A_0^0. The upper-state fundamental frequency which results from this assignment, 3130 cm.$^{-1}$, is a little greater than the known lower-state frequency of the vibration A_{1g}(H), *viz.*, 3062 cm.$^{-1}$. We should expect to find a band 3130 cm.$^{-1}$ above B_0^0. Such a band is present (40616·8 cm.$^{-1}$; intensity 25); but, lying as it does among stronger bands, it was not included in our original list, reproduced in Table I. Since the vibration is totally symmetrical, a band 2 × 3130 cm.$^{-1}$ above A_0^0 might well be visible. Such a band does appear (44869·8 cm.$^{-1}$, intensity 25), but it has an alternative possible explanation.

Progression T consists of two weak bands, the first of which T_0^0, lies 3610 cm.$^{-1}$ above the electronic origin. Two explanations suggest themselves :

$$E_g^+(\text{C } 1)521 + E_g^+(\text{H})3080 = 3601 \text{ cm.}^{-1}; \quad 2 \times E_u^+(\text{C})243 + A_{1g}(\text{H})3130 = 3616 \text{ cm.}^{-1}$$

Either would allow the T bands to gain intensity by resonance with the nearby S bands (Part I, Section 5), and it is possible that the T bands owe their appearance to this effect.

Our study of the series discussed in this Section leads to the following fundamental frequencies of the excited state of benzene :

$$A_{1g}(\text{H})_{\text{excited}} = 3130 \text{ cm.}^{-1} \quad E_g(\text{H } 1)_{\text{excited}} = 3080 \text{ cm.}^{-1}$$

(8) *Band Series* U, W, X, Y, *and* Z.—Several series remain to be discussed which involve the excitation of higher harmonics in the upper electronic state. The series U, which consists of a progression in 923 cm.$^{-1}$, and two short sequences in 161 cm.$^{-1}$, commences with a band, U_0^0, situated 1044 cm.$^{-1}$ above the electronic origin. Our adopted value for the fundamental frequency of the vibration E_g^+(C 1) in the upper electronic state being 521 cm.$^{-1}$, the band U_0^0 can be attributed to a transition between the " vibrationless " level of the electronic ground state and the first overtone level of the E_g^+(C 1) vibration in the electronically excited state.* Such a transition is allowed because of the degenerate character of the vibration (cf. Part I, Section 5).

The weak progression W commences with a band, W_0^0, lying 2070 cm.$^{-1}$ above the electronic origin. From the absence of bands which would otherwise be expected, we infer that the vibrational excitation peculiar to W_0^0 is superposed either on the pure electronic transition, or on the electronic and vibrational transition of the active origin A_0^0. Provisionally adopting the latter view, we find an upper-state frequency 1550 cm.$^{-1}$. It must correspond to total symmetry (Part I, Section 5). Normal co-ordinate calculations having led us to expect (Part XI) that the fundamental frequency of the vibration B_{2g}(H) in the upper electronic state is close to 775 cm.$^{-1}$, we suggest that the upper-state frequency, 1550 cm.$^{-1}$, which appears to characterise series W, may be the first overtone of this vibration. The conclusion is not definite, because, if the vibrational excitation peculiar to W_0^0 were combined only with the electronic transition, then the upper state frequency would be 2070 cm.$^{-1}$, and it would have the symmetry E_g^+; and one could not in that case exclude interpretations involving frequencies of the excited state which are not yet accurately known.

* We have no compelling reason for excluding our former interpretation of the frequency 1044 cm.$^{-1}$ as the fundamental frequency of the planar hydrogen-bending vibration E_g^+(H 2) (cf. *Nature*, 1946, **158**, 163); but we now think that the available evidence in favour of this interpretation is not strong enough to justify its adoption in preference to the explanation given in the text.

The single band X_0^0 lies 1934 cm.$^{-1}$ above the electronic origin. As in the last case, we can infer that a special vibrational excitation of the upper electronic state is involved, which accompanies either the pure electronic transition, or the electronic and vibrational transition characteristic of A_0^0. We provisionally adopt the latter view, having shown by calculation (Part XI) that the fundamental frequency of the vibration E_u^+(H) in the upper electronic state is in the neighbourhood of 706 cm.$^{-1}$; for the upper-state frequency, 1411 cm.$^{-1}$, which then follows from the position of X_0^0, can be simply interpreted (cf. Part I, Section 5) as the first overtone of this vibration. As before, it is not certain that this explanation is unique; for if the vibrational excitation should be directly superposed on the pure electronic transition, the upper-state vibration frequency would be 1934 cm.$^{-1}$; and our present uncertainty with regard to the exact values of certain of the fundamental frequencies of excited benzene would then leave open several possibilities.

The parent band, Y_0^0, of progression Y lies 950 cm.$^{-1}$ above the electronic origin. This position excludes the assumption that the special vibrational excitation which characterises the series is superposed either on the electronic and vibrational transition characteristic of A_0^0, or on that of C_0^0. The strength of the progression makes very improbable any analogous relationship with either B_0^0 or D_0^0. We therefore assume a simple relationship with the electronic origin J_0^0: the transition producing Y_0^0 would start from the " vibrationless " level of the ground state and end on a combination level 950 cm.$^{-1}$ above the " vibrationless " level of the excited state. There are two ways in which, consistently with the selection rules (cf. Part I, Section 5), this frequency could arise. They are as follows:

$$B_{2g}(\mathrm{C})365 + E_{g}^{-}(\mathrm{H})585 = 950 \text{ cm.}^{-1}; \quad E_u^+(\mathrm{C})243 + E_u^+(\mathrm{H})706 = 949 \text{ cm.}^{-1}$$

We incline to the former of these interpretations, largely because of the existence, in the fluorescence spectrum of benzene, of a prominent progression having an analogous explanation in terms of lower-state frequencies (cf. Part III, Section 6).

Finally, mention must be made of a somewhat weak progression labelled Z, which starts with a band, Z_0^0, situated 3885 cm.$^{-1}$ above the electronic origin. The frequencies of the three bands of the Z series are such that they might well belong to the A series. But their intensities, especially that of Z_0^0, seem to suggest separate assignment, although it must be recognised that in the spectral region in which this band appears, it is possible for an illusory band-intensity to be built up by the superposition of a band on an accidental concentration of the overlapped very weak bands which constitute the general background. If a separate assignment is indeed required, then it probably involves a higher harmonic frequency of 3885 cm.$^{-1}$ in the upper electronic state. Possibilities exist for such a harmonic, involving one of the fundamental frequencies which are not yet accurately known; but we make no definite suggestion, in view of the uncertainty as to whether the Z bands should have a separate assignment.

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97. *Excited States of Benzene. Part III. Analysis of the First Ultraviolet Band System of the Fluorescence Spectrum of Benzene.*

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The measurements of Ingold and Wilson on the ultraviolet fluorescence spectrum of benzene are analysed according to the requirements outlined in the abstract of Part I. Cases of apparent Fermi resonance are pointed out. The recognised fundamental frequencies of both combining states are assigned to vibrations.

(1) *Data.*—Measurements on the ultraviolet fluorescence spectrum of benzene have been recorded by Ingold and Wilson (*J.*, 1936, 941, 1210). Following the procedure employed in the treatment of the absorption spectrum, a selection was first made from their long list of measured maxima, of those which appear to be the main maxima of individual bands, as judged from the plates and microphotometer records. These frequencies and the assignments we propose for them are recorded in Tables I, II, and III, which are arranged on the same general plan as Tables I, II, and III of Part II.

The symbolism has been made to correspond as far as possible with that used by Sponer and her collaborators: our series A—D, F, M, and N can be correlated directly with hers. Our fluorescence series A—D, F, and H—N correspond to those absorption series to which the same

TABLE I.

Fluorescence Spectrum of Benzene. Frequencies and Intensities (Ingold and Wilson); and Assignments (cf. Tables II and III).

Freq. ($cm.^{-1}$).	Inty.	Assgnt.	Freq. ($cm.^{-1}$).	Inty.	Assgnt.	Freq. ($cm.^{-1}$).	Inty.	Assgnt.
38612·4	m	A_0^0	36973·6	mw	H_{-1}^0	35402·2	m	$D_{-2}^0; G_{-1}^0$
571·4	w	I_0^0	933·0	w	J_{-1}^1	385·1	ms	Y_{-1}^1
522·4	mw	C_0^0	908·0	m	D_0^2	348·1	ms	$B_{-2}^1; F_{-1}^1$
452·1	mw	A_0^1	895·4	m	N_0^2	321·5	s	
447·5			875·6	w	U_0^0	241·6	mw	$D_{-2}^1; G_{-1}^1$
406·5	mw	B_1^0	840·1	m		218·6	m	$Y_{-1}^2; N_{-2}^0$
365·1	w	C_0^1	831·6	m	B_0^4	184·2	m	$B_{-2}^2; F_{-}^2$
359·5			824·2	m		157·6	ms	
350·2	w	M_0^0	772·5	w	J_{-1}^2	081·1	w	$D_{-2}^2; G_{-1}^2$
344·3			740·3	mw	D_0^4	055·3	mw	$Y_{-1}^3; N_{-2}^1$
338·9			734·7	w	N_0^3	026·3	m	Q_0^0
317·0	w	D_1^0	697·0	w		34996·2	m	$B_{-2}^3; F_{-1}^3$
290·6	mw	A_0^2	683·8	w	B_0^5	894·1	w	$Y_{-1}^4; N_{-2}^2$
284·3			669·0	w		862·0	w	Q_0^1
281·4			657·3	mw	W_0^0	781·9	w	P_{-1}^0
245·0	w	B_1^1	640·6	mw		744·3	w	Y_{-1}^5
204·7	w	C_0^2	625·0	m	A_{-2}^0	702·5	w	Q_0^2
195·5			559·8	ww	$C_{-2}^0; E_{-1}^0$	644·8	w	A_{-4}^0
158·4	ww	D_1^1	538·3	m	Y_0^0	550·0	m	Y_{-2}^0
132·8	w	A_0^3	497·8	s	$B_{-1}^0; F_0^0$	523·6	m	$B_{-2}^0; F_{-2}$
125·3			478·1	s		492·3	ms	
121·8			415·6	m	$D_{-1}^0; G_0^0$	409·6	w	$D_{-2}^0; G_{-2}^0$
084·0	w	B_1^2	388·2	ms		390·6	mw	Y_{-2}^1
046·5	w	C_0^3	336·3	s	$B_{-1}^1; F_0^1$	361·3	mw	$B_{-2}^1; F_{-2}^1$
034·6			317·5	s		328·7	m	
004·7	w	V_0^0	248·8	m	$D_{-1}^1; G_0^1$	250·7	w	$D_{-2}^1; G_{-2}^1$
37991·3	ww	D_1^2	226·7	ms		230·5	mw	$Y_{-2}^2; N_{-3}^0$
966·4	w	H_0^0	216·2	ms	N_{-1}^0	202·6	w	$B_{-2}^2; F_{-2}^2$
961·1		A_0^4	175·6	ms	$B_{-1}^2; F_0^2$	167·3	m	
956·1			156·4	s		090·0	ww	$D_{-2}^2; G_{-2}^2$
945·7			092·9	mw	$D_{-1}^2; G_0^2$	069·1	w	$Y_{-2}^3; N_{-3}^1$
925·8	w	J_0^1	080·3	m		036·5	w	Q_{-1}^0
875·0	ww	C_0^4	064·7	ms		003·7	mw	$B_{-2}^3; F_{-2}^3$
870·5			055·0	m	N_{-1}^1	33908·4	w	Y_{-2}^4
836·6	ww	V_0^1	014·5	m		875·3	ww	Q_{-1}^1
822·3	ww	O_0^0	35996·8	ms	$B_{-1}^3; F_0^3$	792·3	ww	P_{-2}^0
794·5	ww	A_0^5	990·4	ms		711·6	ww	Q_{-1}^2
766·1	w	J_0^2	926·8	mw	$D_{-1}^3; G_0^3$	560·8	w	Y_{-3}^0
616·3	m	A_{-1}^0	899·4	m		536·5	w	$B_{-4}^0; F_{-3}^0$
580·5	w	I_{-1}^0	892·9	mw	N_{-1}^2	499·0	mw	
544·1	ww	$C_{-1}^0; E_0^0$	857·0	mw		419·2	ww	$D_{-4}^0; G_{-3}^0$
528·2	w		832·0	m	$B_{-1}^4; F_0^4$	394·1	ww	Y_{-3}^1
482·5	ss	B_0^0	823·0	m		371·8	ww	$B_{-4}^1; F_{-3}^1$
414·7	w	B_{1-1}^0	789·1	w	P_0^0	334·3	w	
392·2	s	D_0^0	753·7	w	$D_{-1}^4; G_0^4$	256·4	ww	$D_{-4}^1; G_{-3}^1$
320·6	ss	B_0^1	736·1	w		235·5	w	$Y_{-3}^2; N_{-4}^0$
230·1	ms	D_0^1	698·6	w	$B_{-1}^5; F_0^5$	213·9	ww	$B_{-4}^2; F_{-3}^2$
219·0	s	N_0^0	665·6	w		178·8	w	
161·9	s	B_0^2	648·3	w	W_{-1}^0	045·4	ww	Q_{-2}^0
067·8	ms	D_0^2	634·7	mw	A_{-3}^0	013·5	ww	$B_{-4}^3; F_{-3}^3$
059·8	ms	N_0^1	546·6	ms	Y_{-1}^0	32550·3	ww	$B_{-5}^0; F_{-4}^0$
020·3	w	V_{-1}^0	509·4	s	$B_{-2}^0; F_{-1}^0$	511·5	w	
000·3	ms	B_0^3	483·2	s		347·1	ww	$B_{-5}^1; F_{-4}^1$
36990·7	ms							

Note: (1) Intensities are represented by a series of qualitative indications ranging from ww = very weak, through m = medium, etc., to ss = very strong.

(2) The numerical part of the notation in which assignments are expressed is explained in the note below Table I of Part II (p. 419). The letter-symbols used in this Table are defined in the following Tables.

Table II.

Fluorescence Spectrum of Benzene. Key to Series Assignment (cf. Table I).

	Freq. (cm.$^{-1}$).	p'.	p''.	s.
A	= 38090 + 521 − 992p'' − 161s		0—4	0—5
B	= ,, − 608 + 923p' − 992p'' − 161s	0, 1	0—5	0—5
C	= ,, + 2 × 521 − 608 − 992p'' − 161s		0—2	0—4
D	= ,, + 521 − 2 × 608 + 923p' − 992p'' − 161s	0, 1	0—4	0—4
E	= ,, + 2 × 521 − 1600 − 992p''		0, 1	
F	= ,, − 1600 − 992p'' − 161s		0—4	0—5
G	= ,, + 521 − 608 − 1600 − 992p'' − 161s		0—3	0—4
H	= ,, − 608 + 2 × 243 − 992p''		0, 1	
I	= ,, + 2 × 243 − 992p''		0, 1	
J	= ,, − 992p'' − 161s		0, 1	1, 2
M	= ,, + 521 − 265			
N	= ,, − 608 − 265 − 992p'' − 161s		0—4	0—3
O	= ,, − 265			
P	= ,, − 608 − 2 × 849 − 992p''		0—2	
Q	= ,, − 3060 − 992p'' − 161s		0—2	0—2
U	= ,, − 2 × 608			
V	= ,, + 521 − 608 − 992p'' − 161s		0, 1	0, 1
W	= ,, + 521 − 2 × 986 − 992p''		0, 1	
Y	= ,, − 703 − 849 − 992p'' − 161s		0—3	0—5

Table III.

Fluorescence Spectrum of Benzene. Assignment to Vibrations of the Vibration Frequencies (cm.$^{-1}$) contained in Table II.

Upper-state fundamental frequencies (+).	Lower-state fundamental frequencies (−).	Diffs. of upper- and lower-state fundamentals (−).	Vibration.
923	992	69	A_{1g}(C)
—	703	—	B_{2g}(C)
—	986	—	B_{2g}(H)
521	608	87	E_g^+(C 1)
—	1600	—	E_g^+(C 2)
—	3060	—	E_g^+(H 1)
—	243	161	E_u^+(C)
—	849	265	E_g^-(H)

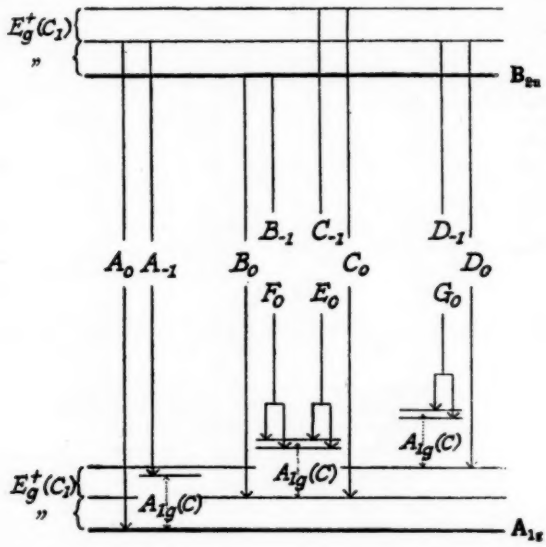
letters are given in Part II, except for the difference that in absorption one observes mainly positive progressions in the upper-state frequency of the totally symmetrical carbon vibration, whereas in fluorescence one finds mainly negative progressions in the lower-state frequency of this vibration. Other fluorescence series, *viz.*, P—Y, also correspond to the absorption series labelled by the same letters, except that, in addition to the difference mentioned, there is now the further difference that at least one non-totally symmetrical vibration enters through its upper-state frequency into the absorption series, and through its lower-state frequency into the fluorescence series.

(2) *Band Series* A—G, U, *and* V.—These series involve the same vibrations as those which control the character of the absorption series A—F, *viz.*, two primary perturbing vibrations, E_g^+(C 1) and E_g^+(C 2), each producing what we call " active origins ", the totally symmetrical vibration, A_{1g}(C), which leads to the main progressions, and the low-frequency vibration, E_u^+(C), which gives rise to the sequences (cf. Part II, Sections 2 and 3).

We may first discuss series A—G, which largely governs the general structure of the spectrum. This spectrum is considerably affected by the already mentioned resonance in the electronic ground state between the combination, E_g^+(C 1)608 + A_{1g}(C)992 = 1600 cm.$^{-1}$, and the fundamental frequency, E_g^+(C 2) = 1600 cm.$^{-1}$. As we know, the resonance causes these energy levels to fall apart by 20 cm.$^{-1}$. With successively added A_{1g}(C) quanta, the resonance splitting becomes repeated, with increasing separations, which amount to 26, 31, 37, and 39 cm.$^{-1}$, respectively, for 1, 2, 3, and 4 extra quanta of the totally symmetrical vibration. (The last of the measured separations is rendered inaccurate by the weakness of the bands.) Because of these splittings the transition corresponding to every band of the negative progressions B and C, which owe their spectral activity to a one-quantum change in the vibration E_g(C 1), excepting only the parent bands B_0 and C_0, will terminate on *both* of a pair of split levels; and likewise, the transitions of all the bands, without exception, of series E and F, which depend on a one-quantum

change in the vibration E_g^+(C 2), will end on the same pairs of split levels. Fig. 1 will make the relationship clear. A similar resonance occurs with one added E_g^+(C 1) quantum, *i.e.*, between the combination $2 \times E_g^+$(C 1)608 + A_{1g}(C)992 = 2208 cm.$^{-1}$, and the combination E_g^+(C 1)608 + E_g^+(C 2)1600 = 2208 cm.$^{-1}$. In this case the splitting amounts to 27 cm.$^{-1}$: whether it increases further with added A_{1g}(C) quanta cannot be determined from the spectrum. It follows that the transitions of bands of the D series, excepting D_0, and, likewise, the transitions of all bands of the G series, must end on pairs of split levels belonging in common to both series. This is also illustrated in Fig. 1.

FIG. 1.



Resonance doublets in fluorescence progressions of benzene.

We can thus understand the general distribution of duplexity amongst the bands. Bands of the A progression are simple, whilst bands of the otherwise analogous progressions B, C, and D each start with a simple band and continue with doublets. Actually a further complication enters, which causes the doublets to develop into triplets higher in the progressions; this, however, is more conveniently discussed later (Section 6). It should be mentioned also that the above discussion applies without modification only to the 0—0 bands of sequences in 161 cm.$^{-1}$; for the higher members of such sequences become split, as has been explained before, by an anharmonicity effect, and these (generally smaller) splittings become superposed on those mentioned above.

A sharp though weak band U_0^0 lies 608 cm.$^{-1}$ below B_0^0. It clearly arises by a transition from the " vibrationless " excited state to the second quantum level of the E_g^+(C 1) vibration in the ground state. The transition is allowed because the vibration is degenerate (cf. Part I, Section 5). Furthermore, although this second quantum level is triple, the transition is allowed to end only on one of its three components : this helps us to understand a sharpness which is not the most common characteristic of quite weak bands.

Series V starts with a band V_0^0 situated 87 cm.$^{-1}$ below the electronic origin, and is associated with a progression in 992 cm.$^{-1}$, and a sequence in 161 cm.$^{-1}$, each of two members. These bands involve 1—1 transitions of the vibration E_g^+(C 1), and are allowed, even though the quantum number does not change, because the vibration is degenerate (cf. Part I, Section 5).

(3) *Band Series* H, I, *and* J.—These series depend on the excitation, in either or both electronic states, of the low-frequency vibration E_u^+(C), whose fundamental frequencies are 404 cm.$^{-1}$ and 243 cm.$^{-1}$ (cf. Part II, Section 4). The series are closely similar to the correspondingly named series of the absorption spectrum; the main differences arise from the fact that, in the downward transitions of fluorescence, different Boltzmann factors modify the intensities.

Series H and I, which commence with bands situated 2×243 cm.$^{-1}$ above the active origin B_0^0, and above the forbidden electronic origin J_0^0, respectively, both involve downward 2—0

transitions of the vibration E_u^+(C). In series H this transition is combined with a 0—1 transition of the activating vibration E_g^+(C 1). Series I, which does not involve the vibration E_g^+(C 1), is nevertheless allowed because the vibration is degenerate (cf. Part I, Section 5). Series J depends on transitions 1—1, 2—2, . . . , of the vibration E_u^+(C), without associated changes in any other non-totally symmetrical vibration. A sequence in 161 cm.$^{-1}$ runs as if from the electronic origin, except that the 0—0 band is missing, and these bands start progressions in 992 cm.$^{-1}$. This series of bands is also allowed because of the degenerate nature of the vibration (*loc. cit.*).

(4) *Band Series* M, N, O, *and* P.—These four series involve the excitation, in one or both electronic states, of a vibration, which, for reasons given in Part XI, we identify as the out-of-plane, hydrogen vibration, E_g^-(H). Its fundamental frequencies in the two states are 849 cm.$^{-1}$ and 585 cm.$^{-1}$ (cf. Part II, Section 6).

Series M and N correspond closely to the identically named series of the absorption spectrum (*loc. cit.*). The band M_0^0 lies 265 cm.$^{-1}$ below A_0^0. We explain it by assuming a 1—1 transition of the vibration E_g^-(H) superposed on the electronic and vibrational transition of A_0^0. The band N_0^0 is similarly related to B_0^0. A weak band O_0^0 appears 265 cm.$^{-1}$ below the forbidden electronic origin : the same band is found in the absorption spectrum (*loc. cit.*). It is explained as arising from a 1—1 transition of the vibration E_g^-(H), without a concomitant change in any other vibration, this type of transition being allowed (cf. Part I, Section 5) on account of the degenerate nature of the vibration E_g^-(H).

The progression P starts with a band P_0^0 displaced 1695 cm.$^{-1}$ below B_0^0, the main active origin for fluorescence. We interpret P_0^0 by assuming a downward 0—2 transition of the vibration E_g^-(H), in combination with the electronic and vibrational transition characteristic of B_0^0. The frequency in the lower electronic state of the first overtone of the vibration E_g^-(H) is thus 1695 cm.$^{-1}$. It can also be directly measured in the Raman spectrum of liquid benzene, and is there 1693 cm.$^{-1}$ (Herzfeld, Ingold, and Poole, *J.*, 1946, 324). Progression P of the absorption spectrum (Part II, Tables I and II) is similar, except that the involved first overtone is that of the upper electronic state.

(5) *Band Series* Q.—An excitation of the degenerate hydrogen-stretching vibration E_g^+(H 1) is responsible for the appearance of this series, which corresponds to the absorption series Q, with the difference that in absorption the activating vibrational excitation takes place in the upper electronic state, while in fluorescence it occurs in the lower state. The origin Q_0^0 of the Q series of the fluorescence spectrum lies 3060 cm.$^{-1}$ below the electronic origin. It is interpreted as arising in a downward 0—1 transition of the vibration E_g^+(H 1). Mention should be made of the fact that the band Q_0^0 coincides with the position in which we might expect to find one of the members of a weak doublet which in our notation would be labelled B_{-2}^2, F_{-1}^2; but a study of the intensities shows that the observed band is not thus explicable, and must represent a new active origin.

The value we obtain, 3060 cm.$^{-1}$, for the fundamental frequency of the vibration E_g^+(H 1) in the electronic ground state differes by 0·4% from the value, 3047 cm.$^{-1}$, given by the Raman spectrum of liquid benzene. The discrepancy is rather larger than usual, but a special reason can be given why the use of liquid benzene for observation of the Raman spectrum might create a relatively large disturbance in the case of this particular vibration. For the frequency lies close to the very strong Raman frequency, 3062 cm.$^{-1}$, belonging to the totally symmetrical vibration, A_{1g}(H). Now, although in the gaseous molecule any interaction between the two vibrations would be completely excluded by their orthogonality, in the liquid substance the intermolecular forces will produce deformations of equilibrium configuration which must entail some loss of orthogonality of the original normal co-ordinates. Accordingly, in the liquid, some dynamical interaction between the vibrations might arise, which could result in a perceptible downward displacement of the weaker frequency. One can well believe that such effects of deformation are more likely to attain considerable magnitudes with hydrogen vibrations than with carbon vibrations, because of the exterior situation of the hydrogen atoms.

(6) *Band Series* W *and* Y.—The series here to be discussed are associated with vibrations of the B_{2g} symmetry class. The parent band, W_0^0, of the progression W lies 1972 cm.$^{-1}$ below the active origin A_0^0, and therefore only 15 cm.$^{-1}$ above the third member of the main A progression, *i.e.*, the band A_{-2}^0. We connect the bands W with the trigonal, out-of-plane, hydrogen vibration, B_{2g}(H). From studies of the infra-red and Raman spectra of benzene and its deuterated derivatives, Herzfeld, Ingold, and Poole concluded (*loc. cit.*) that the fundamental frequency of this vibration (which, actually, is forbidden in the Raman and infra-red spectra of ordinary benzene) is 985 cm.$^{-1}$—quite close, therefore, to the frequency, 992 cm.$^{-1}$, of the carbon

ring-breathing vibration, A_{1g}(C). In fluorescence, the B_{2g}(H) vibration, being non-totally symmetrical and non-degenerate, is not allowed to change by only one quantum; but it can be excited in the lower electronic state by two quanta; and, furthermore, the band which might thus arise would be allowed by the selection rules to intensify itself by resonance at the expense of any close-lying band of the A progression (Part I, Section 5). We suppose that this is what happens; and thus we explain why the first band of the A progression to appear with a prominent companion of the W series is the third member, A^0_{-2}. The value to which we are thus led for the fundamental frequency of the vibration B_{2g}(H), *viz.*, 1972/2 = 986 cm.$^{-1}$, agrees well with the value given by Herzfeld, Ingold, and Poole (985 cm.$^{-1}$).

The presence of a similar progression of companion bands associated with series B cannot be verified because of the resonance splitting which arises in that series (Section 2) : the positions in which the companion bands would be expected are always overlaid by the lower components of the strong B, F doublets. These doublets have, however, a set of companions of still lower frequency with which we must now deal. They are not simply related to the bands just discussed, as can be seen from the fact that they start, not beside the third, but beside the second band of the B progression, B^0_{-1}, that is, beside the first B, F doublet, B^0_{-1}, F^0_0. We call this series Y. It exhibits the peculiar intensity relationship, discussed below, which led to the remark in Section 2 that the higher B, F doublets tend to develop into triplets.

We may first consider the frequencies of the Y bands, the parent of which, Y^0_0, lies 1552 cm.$^{-1}$ below the electronic origin. We interpret this position as indicating a transition from a " vibrationless " excited state to a certain combination level of E^+_g symmetry (cf. Part I, Section 5) in the ground state, *viz.*, the combination B_{2g}(C)703 + E^-_g(H)849 = 1552 cm.$^{-1}$. The fundamental frequency which we are here required to assume for the B_{2g}(C) vibration agrees exactly with the value, 703 cm.$^{-1}$, which Herzfeld, Ingold, and Poole deduced from their studies (*loc. cit.*). The fundamental frequency of the vibration E^-_g(H) is well established (Part II, Section 6). The explanation given makes the Y series of the fluorescence spectrum analogous to series, also called Y, in the absorption spectrum, if our preferred interpretation of the latter be adopted. The absorption series starts with a band 950 cm.$^{-1}$ above the electronic origin, and this we have assumed to arise in a transition from the " vibrationless " ground state to an E^+_g combination of the excited state, *viz.*, the combination B_{2g}(C)365 + E^-_g(H)585 = 950 cm.$^{-1}$. Both involved fundamental frequencies of the upper state have been independently evaluated. It should be mentioned that, since the parent band, Y^0_0, of the fluorescence series lies 2074 cm.$^{-1}$ below A^0_0, it is in the position of a band which could arise from an allowed excitation in the ground state of the first overtone of the vibration E^-_u(H), in combination with the electronic and vibrational transition characteristic of A^0_0; for the fundamental frequency of the vibration E^-_u(H) is 1037 cm.$^{-1}$. However, we exclude this explanation, first, because it could not account for the intensity effects described below, and secondly, because it would lead us to expect a stronger band series, starting with a band equally displaced below B^0_0, whereas in fact no such series appears. The second member of the fluorescence progression, the band Y^0_{-1}, also requires the consideration of another possible explanation. For it happens to lie 3066 cm.$^{-1}$ below A^0_0, that is, in the position of a band which might arise from the allowed excitation, in the ground state, of the fundamental frequency of the hydrogen-stretching vibration A_{1g}(H) (Raman frequency 3062 cm.$^{-1}$), in combination with the electronic and vibrational transition of A^0_0. However, we exclude this interpretation also, for just the same two reasons.

The first band, Y^0_0, of the Y series has only moderate intensity : we judge it to be less than one-tenth as intense as either component of the adjacent B, F doublet, the first band of which lies 40 cm.$^{-1}$ higher, and the second 20 cm.$^{-1}$ higher still. The second Y band, Y^0_{-1}, is considerably stronger than the first, and its relationship to the neighbouring B, F doublet is notably altered. It is about half as strong as the first member of the doublet, which has now become appreciably weaker than the second component. Furthermore, the spacing is altered, the first gap having been reduced to 37 cm.$^{-1}$, and the second gap increased to 26 cm.$^{-1}$. The third band, Y^0_{-2}, is nearly as strong as the first component of the adjacent B, F doublet, the collective intensity of the two bands being roughly the same as the intensity of the second component of the doublet. Again the spacing is altered, so that the first gap is reduced to 26 cm.$^{-1}$, and the second increased to 31 cm.$^{-1}$, the middle band having, so to speak, changed partners. These relationships are approximately repeated, with weaker overall intensities, in the next trio of bands, involving Y^0_{-3}, the first gap being here 24 cm.$^{-1}$, and the second 37 cm.$^{-1}$.

We interpret these facts as indicating a resonance in the lower electronic state between the combination tone, B_{2g}(C) + E^-_g(H), associated with the Y bands, and the already known resonance system, composed from the combination tone, E^+_g(C 1) + A_{1g}(C), and the

fundamental frequency, E_g^+(C 2)—the resonance system responsible for the B, F doublets. The selection rules would allow the postulated additional resonance (Part I, Section 5); for, in every case, those transitions which would produce close-lying bands start from identical levels of the upper state and end on neighbouring levels of the same symmetry in the lower state. Actually, in the case of the first band, Y_0^0, we would assume very little intensification through the allowed resonance with the B_{-1}^0, F_0^0 doublet. The fluorescence band Y_0^0 is of the same order of intensity, relatively to the spectrum as a whole, as is the absorption band, also called Y_0^0, relatively to its spectrum; and in the latter case no question of intensification by resonance can arise. Furthermore, the allowed resonance in the electronic ground state is not strong enough to produce an observed occurrence of the combination tone B_{2g}(C) + E_g^-(H) in the Raman spectrum of benzene, although the resonance doublet frequencies from E_g^+(C 1) + A_{1g}(C) and E_g^+(C 2) appear quite strongly in that spectrum. With successively added A_{1g}(C) quanta, however, a progressively altering situation arises. We have already seen (Section 2) that resonance beomes more effective in separating the energy levels, collectively belonging to E_g^+(C 1) + $(n + 1)A_{1g}$(C) and E_g^+(C 2) + nA_{1g}(C), as n takes on the successive values 0, 1, 2, 3. It follows that, in the progression of doublet levels, one component will approach, more and more closely as n increases, to the theoretical position of the neighbouring combination level B_{2g}(C) + E_g^-(C) + nA_{1g}(C). This is a factor which will open the way to an effective resonance with the last-named combination level; so that transitions from the same initial state which end upon it, and upon that component of the original doublet level which in the main interacts with it, will tend to share intensity. This is how we explain the intensity effects found in the B, F doublets—or in the Y, B, F triplets, if we choose so to call them. The observed intensities suggest that the assumed sharing becomes substantial when $n = 1$, and is already nearly symmetrical when $n = 2$.

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98. *Excited States of Benzene. Part IV. Analysis of the First Ultraviolet Band System of the Absorption Spectrum of Hexadeuterobenzene.*

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The measurements of Sponer on the ultraviolet absorption spectrum of hexadeuterobenzene are analysed as outlined in the abstract of Part I. An attempt is made to assign all the observed bands. A list is given of ten fundamental frequencies of the electronically excited state, and all are assigned to vibrations. Part of the theoretical support for the assignments is given in this paper, and the remainder in Part XI.

(1) *Data.*—The first ultraviolet absorption system of hexadeuterobenzene has been described by Sponer (*J. Chem. Physics*, 1940, **8**, 705). She assigned many bands, and we accept nearly all her assignments. Her list of measured maxima was not so long as those we have already discussed; and, there being no very clear basis for selection, we have copied her complete list and tried to assign all the bands, as shown in Tables I, II, and III.

The notation has been made to agree with hers as far as possible: the band-series A—E, G, and K—N are as named by her. The series A—E, G, H, J, M, N, Q, W, and X correspond to those series in the absorption spectrum of benzene to which we gave the same labels (Part II, Section 1). The other series have less close analogies, or no analogies, with the discussed series in related spectra. Lower-case letters are used to label a few bands, the interpretation of which is more than usually tentative.

(2) *Band Series* A—F *and* F′.—The band series A—D depend on one-quantum changes in the degenerate carbon-bending vibration E_g^+(C 1). As with ordinary benzene (Part II, Section 2), these series form the main framework of the absorption spectrum (cf. Part I, Section 4).

Series E involves a one-quantum excitation in the upper electronic state of the degenerate carbon-stretching vibration E_g^+(C 2). It is relatively somewhat stronger than for benzene, and, as in that case, we assume that it obtains most of its intensity by resonance with the nearby bands of series A (cf. Part II, Section 3). A weak series called F appears, the bands of which lie below those of series E by 80 cm.$^{-1}$. This is the sequence interval, *i.e.*, the difference between the fundamental frequencies of a vibration in the lower and upper electronic states, for the vibration E_g^+(C 1) of hexadeuterobenzene: we conclude that, as compared with E bands, the

TABLE I.

Absorption Spectrum of Hexadeuterobenzene. Frequencies and Intensities (Sponer); and Assignments (cf. Tables II and III).

Freq. (cm.$^{-1}$).	Inty. (25°).	Assgnt.	Freq. (cm.$^{-1}$).	Inty. (−35°).	Assgnt.	Freq. (cm.$^{-1}$).	Inty. (−35°).	Assgnt.
36487	vw	B^2_{-1}	38494·8	w	R^0_0	40271	ew	A^2_2
626·2	m	B^1_{-1}	505·1	w	A^2_0	280	mw	E^2_1
657	vw	L^0_{-1}	514	vw	D^0_1	303	ew	
686	w	D^0_{-1}	533	vw	K^1_0	325	ew	C^1_2
764·6	s	B^0_{-1}	564	w	C^1_0	351·9	mw	B^0_2
			574	vw	M^0_0	375	w	U^0_2
	Inty.		580·6	w		406	w	A^1_2
	(0°)		588·1	w	B^0_1	421·2	m	E^1_1
37278	w	S^1_0	591·9	w		426	ew	
294	w	B^3_0	592·5	w		436·8	mw	
340	ew	D^2_0	647·1	s	A^1_0	441·7	vw	
348	vw		653·7	w		461·8	w	C^0_2
358	ew	N^1_0	676·1	mw	K^0_0	480·3	w	F^0_1
365	vw		705·3	m	C^0_0	498·4	vw	
371	vw		709·3	m		545·5	vs	A^0_2
419·6	m	S^0_0	736	vw	A^0_{1-1}	566·6	s	E^0_1
432·1	m	B^2_0	760·3	w	E^0_{-1}	580·9	m	
460·9	w	L^1_0	787·5	vs	A^0_0	610·5	w	Q^0_0
488·4	m	D^1_0	790·2	vs		630·8	vw	q_0
504·6	m	N^0_0	39056	ew	P^1_0	663	ew	q_0'
508·8	w		067	ew	G^1_0	852	w	X^0_1
540	vw	V^0_0	118	ew	j_1'''	969	ew	G^0_2
548·8	w		190	ew	P^0_0	995	vw	W^0_1
572·2	s	B^1_0	199	vw		41083	vw	F_0'
599·3	m	L^0_0	208	vw	G^0_0	151	w	E^2_2
630·5	m	D^0_0	334	ew	B^1_2	200	w	C^1_3
656·0	w	B^0_{1-1}	372·8	w	R^0_1	233	w	B^0_4
674·4	w	C_6HD_5?	385·4	w	A^2_1	295	mw	E^1_2
712·0	vs	B^0_0	402·9	w	T^0_0	310·6	mw	
720	vw		455·0	w	M^0_1	318	mw	
730	vw	K^0_{-1}	470·4	w	B^0_2	332	ew	C^0_3
765·8	w	C^0_{-1}	502·9	w	U^0_1	357·1	w	F^0_2
797	vw	O^2_0	526·6	s	A^1_1	417·6	mw	A^0_3
844·6	s	A^0_{-1}	533·8	w		440·7	s	E^0_2
872	vw	J^3_0	546·2	w	E^1_0	453·6	m	
939	w	O^1_0	553	w		480·5	mw	Q^0_1
986·2	mw	H^1_0	566·4	mw		502·5	vw	q_1
38001·8	m	J^2_0	587·7	m	C^0_1	530	ew	q_1'
010·5	mw		609·3	vw	F^0_0	555	ew	q''
044·0	w	j^1	669·0	vs	A^0_1	728	vw	X^0_2
085·9	m	O^0_0	693·4	s	E^0_0	773	ew	q'''
095·1	w	I^0_0	706·6	m		961	ew	F_1'
126·7	m	H^0_0	953	ew	X^0_0	42198	ew	E^1_3
150·3	s	J^1_0	973	ew		326	m	E^0_3
185·1	m	j^0	40093	ew	G^0_1	348	m	Q^0_2
205	m	j'	120	ew	W^0_0	373	ew	q_2
220·0	m	j''	146	ew	N^0_3	390	ew	q_2'
242	m	j_0'''	181	ew	C^2_2	43195	w	E^0_4
			213	ew	B^1_3	220	vw	Q^0_3

Notes.—(1) The temperatures in the column of intensities are those of saturated vapour at the pressure in the absorption tube. The intensity indications (ranging from vs = very strong to ew = extremely weak) are to be judged with reference to these temperatures.

(2) The significance of the numerical parts of the symbols in the column of assignments is explained under Table I of Part II (p. 419). The letter symbols in this Table are defined in the following tables.

TABLE II.

Absorption Spectrum of Hexadeuterobenzene. Key to Assignments (cf. Table I).

	Freq. (cm.$^{-1}$).	p'.	p''.	s.
A	= 38290 + 499 + 879p' − 943p'' − 141s	0—3	0, 1	0—2
B	= ,, − 579 + 879p' − 943p'' − 141s	0—4	0, 1	0—3
C	= ,, + 2 × 499 − 579 + 879p' − 943p'' − 141s	0—3	0, 1	0—2
D	= ,, + 499 − 2 × 579 + 879p' − 943p'' − 141s	0, 1	0, 1	0—2
E	= ,, + 1403 + 879p' − 943p'' − 141s	0—4	0, 1	0—2
F	= ,, + 499 − 579 + 1403 + 879p'	0—2		
F′	= ,, + 2 × 1403 + 879p'	0, 1		
G	= ,, + 499 + 2 × 208 + 879p' − 141s	0—2		0, 1
H	= ,, − 579 + 2 × 208 − 141s			0, 1
I	= ,, + 499 − 2 × 350			
J	= ,, − 141s			1—3
j	= ,, − 105 − 141s			0, 1
j′	= ,, − 85			
j″	= ,, − 70			
j‴	= ,, − 48 + 879p'	0, 1		
K	= ,, + 499 − 114 − 943p'' − 141s		0, 1	0, 1
L	= ,, − 579 − 114 − 943p'' − 141s		0, 1	0, 1
M	= ,, + 499 − 208 + 879p'	0, 1		
N	= ,, − 579 − 208 + 879p' − 141s	0, 3		0, 1
O	= ,, − 208 − 141s			0—2
P	= ,, + 2 × 454 − 141s			0, 1
Q	= ,, + 2320 + 879p'	0—3		
q	= ,, + 2340 + 879p'	0—2		
q′	= ,, + 2372 + 879p'	0—2		
q″	= ,, + 3265			
q‴	= ,, + 3483			
R	= ,, + 499 − 295 + 879p'	0, 1		
S	= ,, − 579 − 295 − 141s			0, 1
T	= ,, + 499 + 2 × 306			
U	= ,, + 499 − 165 + 879p'	1, 2		
V	= ,, − 579 − 165			
W	= ,, + 499 + 2 × 663 + 879p'	0, 1		
X	= ,, + 499 + 2 × 590 + 879p'	0—2		

Note: The frequency 38290 cm.$^{-1}$ is that of the electronic origin. The other frequencies are vibration frequencies, and they are assigned to vibrations in Table III. Concerning the frequencies 105, 85, 70, 48, 2340, 2372, 3265, and 3483 cm.$^{-1}$, see text (Sections 4 and 7).

TABLE III.

Absorption Spectrum of Hexadeuterobenzene. Assignment to Vibrations of the Vibration Frequencies (cm.$^{-1}$) contained in Table II.

Upper-state fundamental frequencies (+).	Lower-state fundamental frequencies (−).	Diffs. of upper- and lower-state fundamentals (−).	Vibration.
879	943	64	A_{1g}(C)
(382)	—	114	A_{2u}(H)
306	—	295	B_{2g}(C)
663	—	165	B_{2g}(H)
499	579	80	E_g^+(C 1)
1403	—	—	E_g^+(C 2)
2320	—	—	E_g^+(H 1)
(830)	—	—	E_g^+(H 2)
208	350	141	E_u^+(C)
590	—	—	E_u^+(H)
454	—	208	E_g^-(H)

Note: Concerning the frequencies 382 cm.$^{-1}$ and 830 cm.$^{-1}$, see text (Sections 5 and 11).

F bands have one additional quantum of this vibration in each of the combining states. Thus series F is related to E, just as D is to B, or as C is to A.

Generally, the series here discussed display progressions in the totally symmetrical vibration, A_{1g}(C). They are mainly positive in the interval 879 cm.$^{-1}$, but the beginnings of negative progressions in 943 cm.$^{-1}$ can also be seen. The stronger bands of the progressions are the

starting points of negatively-running sequences in the low frequency vibration $E_u^+(C)$, the sequence interval for this vibration of hexadeuterobenzene being 141 cm.$^{-1}$.

These bands, and analogous bands of the fluorescence spectrum (Part V, Section 2), determine the electronic origin for hexadeuterobenzene,

$$J_0^0 = 38290 \pm 1 \text{ cm.}^{-1},$$

as well as the following vibration frequencies:

$A_{1g}(C)_{ground} = 943$ cm.$^{-1}$ $\quad$ $A_{1g}(C)_{excited} = 879$ cm.$^{-1}$

$E_g^+(C\ 1)_{ground} = 579$ cm.$^{-1}$ $\quad$ $E_g^+(C\ 1)_{excited} = 499$ cm.$^{-1}$

$E_g^+(C\ 2)_{excited} = 1403$ cm.$^{-1}$ $\quad$ $E_u^+(C)_{ground} - E_u^+(C)_{excited} = 141$ cm.$^{-1}$

The fundamental frequencies of the electronic ground state, as thus determined, agree satisfactorily with the values given by the Raman spectrum of liquid hexadeuterobenzene, *viz.*, $A_{1g}(C) = 943{\cdot}2$ cm.$^{-1}$, and $E_g^+(C\ 1) = 577{\cdot}4$ cm.$^{-1}$ (Poole, *J.*, 1946, 245).

A weak progression, called F′, consists of a band lying 2793 cm.$^{-1}$ above the electronic origin, followed by a second band after the usual interval 879 cm.$^{-1}$. We associate these bands with a transition, which starts from the " vibrationless " ground state, and involves the excitation in the upper electronic state of two quanta of the degenerate carbon-stretching vibration $E_g^+(C\ 2)$. Such transitions are allowed on account of the degenerate nature of the vibration (Part I, Section 5).

(3) *Band Series* G, H, I, *and* J.—These series depend especially on the low-frequency vibration, $E_u^+(C)$. Series G and H, which start with bands lying 416 cm.$^{-1}$ above A_0^0 and B_0^0, involve the excitation in the upper electronic state of two quanta of this vibration, in combination with the electronic and vibrational transitions characteristic of series A and B respectively. The sequences in 141 cm.$^{-1}$, which are contained in series G and H, therefore involve upward transitions of the type 0—2, 1—3, . . ., in the vibration $E_u^+(C)$.

In the single band I_0^0, lying 695 cm.$^{-1}$ below A_0^0, we observe the loss of two ground-state quanta of the vibration $E_u^+(C)$ in an upward 2—0 transition, which takes place in combination with the electronic and vibrational transitions characteristic of A_0^0. Lower-state overtone frequencies are seldom observed in the absorption spectra of benzenes, but here the very low value of the frequency renders the Boltzmann factor less inhibitory than usual.

On account of the degenerate nature of the vibration $E_u^+(C)$ we are allowed to observe the excitation of two of its upper-state quanta, in combination with the electronic transition, but without associated changes in any other non-totally symmetrical vibration (cf. Part I, Section 5). This is actually observed in the absorption spectrum of ordinary benzene (cf. Part II, Section 4). A corresponding observation with hexadeuterobenzene is, however, precluded, because the bands which would be thus produced would coincide with the strong bands of series C.

The degeneracy of the vibration $E_u^+(C)$ also permits the occurrence, in combination with the electronic transition, of 1—1, 2—2, and, in general, n—n transitions of this vibration (provided that $n \neq 0$), without associated changes in any other non-totally symmetrical vibration. Such transitions give rise to the series, called J, which is found in the absorption and fluorescence spectra of ordinary benzene (Part II, Section 4; Part III, Section 3). A similar series, also called J, is found in the absorption (and in the fluorescence) spectrum of hexadeuterobenzene. It appears as a negatively running sequence in 141 cm.$^{-1}$, which starts as if from the electronic origin, except that the 0—0 band is missing.

From all these bands, and from analogous bands of the fluorescence spectrum (Part V, Section 3), we deduce the following fundamental frequencies of hexadeuterobenzene:

$$E_u(C)_{ground} = 350 \text{ cm.}^{-1} \qquad E_u(C)_{excited} = 208 \text{ cm.}^{-1}$$

The ground-state frequency agrees well with other estimates. This fundamental frequency is forbidden in both Raman and infra-red spectra, but Poole has recently observed it in the Raman spectrum of liquid hexadeuterobenzene, its weak appearance there being evidently due to the perturbing effect of cohesive forces. His observed frequency was 350 cm.$^{-1}$ (*loc. cit.*). Herzfeld, Ingold, and Poole estimated this frequency from combination tones in the Raman and infra-red spectra of hexadeuterobenzene. Their value is 352 cm.$^{-1}$ (*J.*, 1946, 316).

(4) *Band Series* j, j′, j″, j‴.—Between the 1—1 band of the J sequence and the electronic origin lie four weak bands, separated from the latter by the intervals 105, 85, 70, and 48 cm.$^{-1}$.

Two of them appear to have companions displaced either by the positive progression interval, 879 cm.$^{-1}$, or by the negative sequence interval, 141 cm.$^{-1}$. No definite assignments are suggested for these bands, and all we seek to show is that they are not incapable of being plausibly interpreted.

Three of them have allowed explanations (cf. Part I, Section 5) as combinations, involving not more than two vibrational quanta in either electronic state, of frequencies otherwise determined. They are as follows:

$$\mathrm{j} = \begin{cases} \mathrm{J}_0^0 - E_g^+(\mathrm{H}\ 2)867 + B_{2g}(\mathrm{C})306 + E_g^-(\mathrm{H})454 = \mathrm{J}_0^0 - 107\ \mathrm{cm.}^{-1} \\ \mathrm{J}_0^0 - E_u^-(\mathrm{H}\ 1)813 + E_g^+(\mathrm{C}\ 1)499 + E_u^+(\mathrm{C})208 = \mathrm{J}_0^0 - 106\ \mathrm{cm.}^{-1} \end{cases}$$

$$\mathrm{j}' = \mathrm{J}_0^0 - E_u^+(\mathrm{H})793 + E_g^+(\mathrm{C}\ 1)499 + E_u^+(\mathrm{C})208 = \mathrm{J}_0^0 - 86\ \mathrm{cm.}^{-1}$$

$$\mathrm{j}'' = \mathrm{J}_0^0 - E_g^-(\mathrm{H})662 + A_{2u}(\mathrm{H})382 + E_u^+(\mathrm{C})208 = \mathrm{J}_0^0 - 72\ \mathrm{cm.}^{-1}$$

The fourth, $\mathrm{j}''' = \mathrm{J}_0^0 - 48$ cm.$^{-1}$, might have an explanation of the same general form, but involving one of the not accurately known upper-state fundamental frequencies, for instance, one of the four planar deuterium-bending frequencies.

Alternatively, any of the bands might represent a 1—1 transition of some degenerate vibration for which the Boltzmann factor is not prohibitively small. An interpretation of $\mathrm{j}' = \mathrm{J}_0^0 - 85$ cm.$^{-1}$ as a 1—1 transition of the vibration $E_g^+(\mathrm{C}\ 1)$, unaccompanied by any other vibrational change, cannot be excluded. And any of the other bands might have a similar explanation involving 1—1 transitions of one of the degenerate deuterium-bending vibrations, $E_g^+(\mathrm{H}\ 2)$ and $E_u^-(\mathrm{H}\ 1)$, whose frequencies in the upper electronic state we do not yet know with precision.

(5) *Band Series* K *and* L.—One of the most striking qualitative differences between the absorption spectra of benzene and of hexadeuterobenzene is the following. In both spectra the recurrent gaps of 161 cm.$^{-1}$ or 141 cm.$^{-1}$ between the stronger bands of both series A and B are each cut into two roughly equal parts by the somewhat weaker bands of series C and D respectively. But in the hexadeuterobenzene spectrum every gap of 141 cm.$^{-1}$ belonging to series A and B is further divided, now about three-quarters down, by a band which is not very much weaker than the half-way band. The three-quarter-way bands associated with series A form series K, and those belonging to series B form series L. Each K or L band lies 114 cm.$^{-1}$ below an A or B band.

Sponer has already suggested that these K and L bands involve 1—1 transitions of some vibration superposed upon the transitions characteristic of A or B bands. Strong evidence for the correctness of this view is afforded by comparison with the fluorescence spectrum (Part V, Section 4). Here the K and L bands again appear, with approximately the same intensities relative to the now-altered intensities of the associated A and B bands, and with the same negatively directed displacement of 114 cm.$^{-1}$, even though the main progressions run the opposite way to what they do in absorption.

For reasons given in an accompanying paper (Part XI), we assign these bands to excitations in each electronic state of the hexagonal, out-of-plane vibration $A_{2u}(\mathrm{H})$. The interval 114 cm.$^{-1}$ then represents the difference between the fundamental frequencies of this vibration in the lower and upper electronic states.

It is probable that the first overtone of this vibration in the upper electronic state is involved in a progression, which is not separately assigned in Table I, because of the difficulty of being sure that the bands concerned are really separate from some neighbouring broad bands of the E series. If we should assign this progression separately, the first band would lie 763 cm.$^{-1}$ above the main origin A_0^0, the interval, 763 cm.$^{-1}$, corresponding to the upper-state overtone frequency. From these assignments, the following fundamental frequencies may be derived:

$$A_{2u}(\mathrm{H})_{\mathrm{ground}} = 496\ \mathrm{cm.}^{-1} \qquad A_{2u}(\mathrm{H})_{\mathrm{excited}} = 382\ \mathrm{cm.}^{-1}$$

The fundamental frequency for the electronic ground state agrees with the value, 496·5 cm.$^{-1}$, observed by Bailey, Carson, and Ingold as the frequency of the long-wave fundamental band in the infra-red spectrum of hexadeuterobenzene vapour (*J.*, 1946, 252). Both the frequencies are well confirmed by the fluorescence spectrum (cf. Part V, Section 4).

It has to be explained why bands corresponding to the K and L bands of hexadeuterobenzene are not observed in either the absorption or the fluorescence spectrum of benzene. Of course, a rather smaller Boltzmann factor will apply to benzene. But the main reason, we believe, is that the sequence interval of the $A_{2u}(\mathrm{H})$ vibration of benzene is so close to 161 cm.$^{-1}$, that the

expected bands are obscured under the 1—1 bands of the E_u^+(C) sequences. On the other hand, the benzene progression corresponding to the difficultly verifiable overtone progression of hexadeuterobenzene is readily observed in the absorption spectrum of benzene, its position there being favourable for observation.

(6) *Band Series* M, N, O, *and* P.—Series M and N consist of a number of bands of considerable intensity each situated 208 cm.$^{-1}$ below one of the stronger bands of series A and B. Sponer has suggested (*loc. cit.*) that these bands involve 1—1 transitions of some vibration, in combination with the electronic and vibrational transitions characteristic of A or B bands. As before, comparison with the fluorescence spectrum (Part V, Section 5) well supports this view.

Partly on the internal evidence of the spectrum, and partly from comparisons between different spectra (Part XI) we assign the interval 208 cm.$^{-1}$ as the difference between the fundamental frequencies of the vibration E_g^-(H) in the two electronic states. This vibration being degenerate, its 1—1 transitions need not be accompanied by other vibrational changes (Part I, Section 5). Consistently, we find the interval 208 cm.$^{-1}$ appearing in series O as a negative displacement from the electronic origin. Series O is present also in the fluorescence spectrum (Part V, Section 5).

The degeneracy of the vibration would also permit the excitation of its first overtone without accompanying vibrational changes (*loc. cit.*). Consistently, we find in the absorption spectrum a series called P, which starts with a band 909 cm.$^{-1}$ above the electronic origin, the interval 909 cm.$^{-1}$ being evidently the upper-state overtone frequency.

These assignments enable us to deduce the following fundamental frequencies:

$$E_g^-(\mathrm{H})_{\mathrm{ground}} = 662 \text{ cm.}^{-1} \qquad E_g^-(\mathrm{H})_{\mathrm{excited}} = 454 \text{ cm.}^{-1}$$

The fundamental frequency in the electronic ground state, as given by the Raman spectrum of liquid hexadeuterobenzene, is 661·7 cm.$^{-1}$ (Poole, *loc. cit.*). Both the frequencies are well confirmed by the fluorescence spectrum (Part V, Section 5).

It is not impossible that some part of the intensity of the bands of series M, N, and O, in either absorption or fluorescence or both, may be due to 1—1 transitions of the vibration E_u^-(H), since the difference between the fundamental frequencies of this vibration in the lower and upper electronic states happens to be quite close to 208 cm.$^{-1}$. The Boltzmann factors would be smaller for this vibration (cf. Section 10).

(7) *Band Series* Q, q, q′, q″, *and* q‴.—Progression Q, the parent band of which lies 2320 cm.$^{-1}$ above the electronic origin, is the most prominent of the progressions occupying the high-frequency end of the absorption spectrum of hexadeuterobenzene. Obviously this series is to be correlated with the series, also called Q, in the absorption spectrum of benzene. We therefore assign the hexadeuterobenzene series in the same way as the benzene series, assuming the parent band Q_0^0 to involve transitions from the " vibrationless " level of the electronic ground state to the one-quantum level of the E_g^+ hydrogen-stretching vibration in the electronically excited state. This assignment gives the following fundamental frequency of the upper state:

$$E_g^+(\mathrm{H}\ 1)_{\mathrm{excited}} = 2320 \text{ cm.}^{-1}$$

The bands of the Q series in the hexadeuterobenzene spectrum are accompanied by a fairly regular pattern of weak satellites. Those which lie 20 cm.$^{-1}$ above the Q bands constitute series q, and the very weak ones 52 cm.$^{-1}$ above the Q bands form series q′; a single very weak band 75 cm.$^{-1}$ above one of the Q bands is called q″. We think that these bands represent combination frequencies which have gained intensity by resonance with the neighbouring Q bands, and, except for this, would probably have been unobservably weak. For each satellite series, several possible explanations exist, each requiring the assumption of some plausible value of an upper-state frequency which is not exactly known—a fundamental of one of the symmetry classes, A_{2g}, B_{2u}, and E_u^-. The alternative interpretations are too hypothetical to list, but we give as example, the following explanation, in which the first of the involved fundamental frequencies is independently determined (Part XI), whilst the second is chosen to fit:

$$\mathrm{q}'' = \mathrm{J}_0^0 + 940(B_{1u}) + 2325(E_u^-)$$

All that can really be said of the second component frequency is that, since it is the fundamental frequency of a deuterium-stretching vibration, it must be close to the known E_g^+ frequency, 2320 cm.$^{-1}$.

A further weak high-frequency band called q‴ lies 1163 cm.$^{-1}$ above Q_0^0. No well-supported

assignment can be given, but it may be noted that the band might be attributed to the excitation, in combination with the electronic and vibrational transition of Q_0^0, of the first overtone of the vibration E_u^+(H), the fundamental frequency of which, as otherwise determined, is 590 cm.$^{-1}$.

(8) *Band Series* R, S, *and* T.—Series R and S commence with bands, R_0^0 and S_0^0, lying 295 cm.$^{-1}$ below the active origins A_0^0 and B_0^0 respectively. As with some of the series considered in Sections 5 and 6, we suppose series R and S to involve 1—1 vibrational transitions, superposed on the electronic and vibrational transitions characteristic of series A and B respectively. The interval 295 cm.$^{-1}$ is, then, the difference between the fundamental frequencies of some vibration in the lower and upper electronic states. Comparison with the fluorescence spectrum (Part V, Section 7), in which the same displacements are found in association with oppositely running progressions, gives strong support to this interpretation.

We identify the vibration concerned as the trigonal, out-of-plane vibration, B_{2g}(C) (cf. Part XI). To it we also relate the series T, represented in Table I by the single band T_0^0, although in fact this may start a progression, the upper members of which we do not assign, because of the difficulty of being sure that they are distinct from some neighbouring, complex bands of series E. The band T_0^0 lies 613 cm.$^{-1}$ above the main active origin A_0^0, and we interpret the interval as the first overtone in the upper electronic state of the vibration B_{2g}(C).

These assignments, supported by others relating to the fluorescence spectrum, lead to the following fundamental frequencies :

$$B_{2g}(\mathrm{C})_{\mathrm{ground}} = 601 \text{ cm.}^{-1} \qquad B_{2g}(\mathrm{C})_{\mathrm{excited}} = 306 \text{ cm.}^{-1}$$

This fundamental vibration is forbidden in the infra-red and Raman spectra, but a study of these spectra of certain partly deuterated benzenes, and of higher harmonic frequencies in the spectra of hexadeuterobenzene, led Herzfeld, Ingold, and Poole (*loc. cit.*) to assign the value 601 cm.$^{-1}$ as the fundamental B_{2g}(C) frequency of the ground state of hexadeuterobenzene.

(9) *Band Series* U, V, *and* W.—Series U and V comprise a number of weak bands negatively displaced by a common interval, 165 cm.$^{-1}$, from the stronger bands of series A and B respectively. The U and V bands are always overlapped by the relatively strong bands displaced by the ubiquitous interval, 141 cm.$^{-1}$, from the same A and B bands. Doubtless for this reason, the first band, U_0^0, of the U progression, overlapped as it is by the strong band A_0^1, has not been measured in the absorption spectrum. However, it has been measured (38625·3 cm.$^{-1}$) in the fluorescence spectrum (Part V, Table I). We explain series U and V by assuming a 1—1 vibrational transition, in combination with the electronic and vibrational transitions characteristic of series A and B respectively. Comparison with the fluorescence spectrum, where we find the same interval in association with oppositely running progressions, gives strong support to this interpretation (Part V, Section 8). The interval 165 cm.$^{-1}$ is, then, the difference between the fundamental frequencies of some vibration in the two electronic states.

For reasons given later, we identify the vibration involved as the trigonal, out-of-plane vibration B_{2g}(H) (cf. Part XI). To the same vibration we relate the series W, the parent band of which, W_0^0, lies 1326 cm.$^{-1}$ above the main active origin A_0^0. This interval we regard as the first overtone of the vibration B_{2g}(H) in the upper electronic state.

From these assignments, and others related to the fluorescence spectrum, we may deduce the following fundamental frequencies :

$$B_{2g}(\mathrm{H})_{\mathrm{ground}} = 828 \text{ cm.}^{-1} \qquad B_{2g}(\mathrm{H})_{\mathrm{excited}} = 663 \text{ cm.}^{-1}$$

The ground-state value agrees with the value, 827 cm.$^{-1}$, derived by Herzfeld, Ingold, and Poole (*loc. cit.*) by the methods mentioned above in connexion with the B_{2g}(C) vibration (preceding Section).

(10) *Band Series* X.—The three observed bands of this progression lie positively displaced by 1180 cm.$^{-1}$ from the three strongest bands of series A. The common interval is evidently an upper-state frequency of total symmetry, excited in combination with the electronic and vibrational transitions characteristic of series A. For reasons given later (Part XI) we assign the interval as the first overtone of out-of-plane degenerate vibration E_u^+(H). The fundamental frequency which results from this assignment is as follows :

$$E_u^+(\mathrm{H})_{\mathrm{excited}} = 590 \text{ cm.}^{-1}$$

We were not able to find, in either the absorption or the fluorescence spectrum of hexadeuterobenzene, any distinct bands displaced from A or B bands by the sequence interval of this

vibration. This may be due in part to the proximity of the sequence interval to that of the vibration E_g^-(H), *viz.*, 208 cm.$^{-1}$. Possibly 1—1 transitions of the vibration E_u^+(H) contribute to the intensity of those bands which arise mainly from 1—1 transitions of the vibration E_g^-(H) (cf. Section 6). The fundamental frequency E_u^+(H) of the electronic ground state has been determined by Herzfeld, Ingold, and Poole (*loc. cit.*), largely from combination tones in the Raman and infra-red spectra of hexadeuterobenzene. Their value is 793 cm.$^{-1}$.

(11) *The Bands at* 39118 *and* 39953 *cm.*$^{-1}$.—Sponer (*loc. cit.*) has very reasonably suggested that the band at 39118 cm.$^{-1}$ might be assigned to a transition from the " vibrationless " ground state to the one-quantum level of the planar deuterium-bending vibration, E_g^+(H 2), in the upper electronic state. This transition is allowed by the selection rules. It must also be remarked that the band at 39953 cm.$^{-1}$, instead of being part of a doublet structure attributed to the band X_0^0 in Table I, might arise from a transition from the " vibrationless " ground state to the two-quantum level of the vibration, E_g^+(H 2), in the upper electronic state. This transition would also be allowed by the selection rules. These assignments, necessarily tentative, lead to the following upper-state fundamental frequency:

$$E_g^+(\text{H } 2)_{\text{excited}} = 830 \text{ cm.}^{-1}$$

The corresponding ground-state frequency, as given in the Raman spectrum of liquid hexadeuterobenzene, is 867·3 cm.$^{-1}$ (Poole, *loc. cit.*). Indications of a closely similar planar deuterium-bending frequency of the upper electronic state are found in the absorption spectrum of 1 : 3 : 5-trideuterobenzene (Part VI, Section 4).

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99. *Excited States of Benzene. Part V. Analysis of the First Ultraviolet Band System of the Fluorescence Spectrum of Hexadeuterobenzene.*

By Francesca M. Garforth and Christopher K. Ingold.

The measurements of Ingold and Wilson on the ultraviolet fluorescence spectrum of hexadeuterobenzene are analysed as outlined in the abstract of Part I. A number of fundamental frequencies of both electronic states are recognised, and are assigned to their vibrations.

(1) *Data.*—The ultraviolet fluorescence spectrum of hexadeuterobenzene has been studied experimentally by Ingold and Wilson (*J.*, 1936, 941, 1210). In analysing their data, we have followed the procedure adopted in the case of the fluorescence spectrum of benzene, including the re-examination of original plates and microphotometer records (cf. Part III, Section 1). The results of this analysis are set out in Tables I, II, and III, which are arranged like the corresponding tables in the preceding papers.

The notation applied to the various series has been made to agree as closely as possible with that used for the fluorescence spectrum of benzene, and for the absorption spectrum of hexadeuterobenzene. The following identically named series correspond in the fluorescence spectra of benzene and hexadeuterobenzene in the closest way possible, *viz.*, that the same vibrations enter in the same manner into each, although, of course, the actual frequencies are different: A, B, C, D, H, J, M, N, O, P, Q. The following identically named series correspond in the absorption and fluorescence spectra of hexadeuterobenzene in the closest possible way, *viz.*, that all non-totally symmetrical vibrations enter in the same way, and with the same frequencies, into each, the only difference being that the totally symmetrical progressions run mainly towards the positive direction in absorption and towards the negative in fluorescence: A, B, C, D, H, J, K, L, M, N, O, R, S, U, V. The following identically named series also correspond in the absorption and fluorescence spectra of hexadeuterobenzene, but less closely, the further difference being that a non-totally symmetrical vibration enters into the absorption spectrum through the excitation of one quantum in the upper electronic state and into the fluorescence spectrum through a similar excitation in the electronic ground state: I, Q, T.

TABLE I.

Fluorescence Spectrum of Hexadeuterobenzene. Frequencies and Intensities (Ingold and Wilson); and Assignments (cf. Tables II and III).

Freq. (cm.$^{-1}$).	Inty.	Assgnt.	Freq. (cm.$^{-1}$).	Inty.	Assgnt.	Freq. (cm.$^{-1}$).	Inty.	Assgnt.
38789·1	m	A_0^0	37502·7	m	N_0^0	36207·4	w	B_{-1}^4
737·3	ww	A_{1-1}^0	486·3	m	D_0^1	191·4	w	S_{-1}^3
709·8	mw	C_0^0	459·4	w	L_0^1	064·0	ww	B_{-1}^5
672·7	w	K_0^0	430·4	ms	B_0^2	047·8	ww	S_{-1}^4
653·9	w	A_0^1	418·4	ms	S_0^0	014·3	w	Q_0^0
647·1	m		373·5	w	N_0^1	35957·5	ww	A_{-3}^0
625·3	ww	U_0^0	362·5	w		934·8	w	X_0^0
616·4	ww	P″	352·1	w	D_0^2	928·7	w	
588·5	mw	B_1^0	346·5	w		878·2	ww	Q_0^1
581·2	mw	M_0^0	291·1	m	B_0^3	852·8	ww	W_{-1}^0
569·0	mw	C_0^1	276·3	m	S_0^1	825·2	ms	B_{-2}^0
563·5	w		224·0	ww	N_0^2	778·3	ww	F_{-1}^0
532·7	ww	K_0^1	216·4	ww	D_0^3	763·2	ww	B_{1-2}^0
503·4	mw	A_0^2	211·8	ww		748·2	w	D_{-2}^0
493·0	mw	R_0^0	150·1	w	B_0^4	717·2	ww	L_{-2}^0
474·9	w	G_0^0	133·7	w	S_0^2	684·7	m	B_{-2}^1
446·5	w	B_1^1	016·1	ww	B_0^5	618·8	mw	N_{-2}^0
436·5	w	M_0^1	011·1	ww		604·6	w	D_{-2}^1
427·4	w	C_0^2	004·8	ww	I_0^0	577·1	ww	L_{-}^1
416·2	ww		36990·5	ww	S_0^3	560·4	ww	Y_{-1}^0
409·3	ww		965·7	ww	P′	554·6	ww	
368·5	w	A_0^3	898·7	w	A_{-2}^0	544·3	mw	B_{-2}^2
352·8	ww	R_0^1	888·1	ww		533·9	w	S_{-}^0
322·8	ww	T_0^0	877·2	ww		478·5	ww	N_{-2}^1
311·6	ww	B_1^2	845·0	ww	A_{1-3}^0	470·3	ww	D_{-2}^2
300·4	ww	M_0^2	824·2	ww	C_{-2}^0	426·6	ww	Z_0^0
286·6	ww	C_0^3	800·4	ww	W_0^0	402·4	ww	B_{-2}^3
147·1	ww	J_0^1	766·9	ss	B_{-1}^0	391·3	ww	S_{-2}^1
141·6	ww		716·9	w	F_0^0	245·9	ww	S_{-2}^2
124·4	ww	H_0^0	704·8	w	B_{1-2}^0	069·7	mw	Q_{-1}^0
085·5	ww	O_0^0	686·7	m	D_{-1}^0	014·3	ww	A_{-4}^0
078·4	ww		656·1	mw	L_{-1}^0	34990·5	w	X_{-1}^0
007·2	w	J_0^2	626·5	s	B_{-1}^1	930·7	ww	Q_{-1}^1
37999·9	w		560·0	m	N_{-1}^0	906·1	ww	W_{-2}^0
984·8	w	H_0^1	545·1	m	D_{-1}^1	884·5	mw	B_{-3}^0
947·1	ww	O_0^1	511·6	ww	L_{-1}^1	744·5	w	B_{-3}^1
933·9	ww		500·2	ww	Y_0^0	682·8	ww	N_{-3}^0
871·5	ww	J_0^3	486·4	m	B_{-1}^2	602·0	ww	B_{-3}^2
841·4	m	A_{-1}^0	476·1	m	S_{-1}^0	592·7	ww	S_{-3}^0
795·1	ww	E_0^0	421·4	w	N_{-1}^1	482·3	ww	Z_{-1}^0
783·4	ww	A_{1-2}^0	406·3	w	D_{-1}^2	117·3	ww	Q_{-3}^0
764·5	w	C_{-1}^0	388·1	ww	P	33969·4	ww	W_{-3}^0
727·1	ww	K_{-1}^0	362·8	ww	Y_0^1	944·2	w	B_{-4}^0
709·4	ss	B_0^0	346·3	mw	B_{-1}^3	789·1	ww	B_{-4}^1
628·8	m	D_0^0	332·4	mw	S_{-1}^1	737·2	ww	N_{-4}^0
597·1	mw	L_0^0	278·5	ww	N_{-1}^2	644·3	ww	S_{-4}^0
570·1	s	B_0^1	269·0	ww	D_{-1}^3	004·6	ww	B_{-5}^0
548·4	w	V_0^0						

Note: The intensity symbols, and the numerical parts of the assignment symbols are explained in the notes beneath Table I of Part III (p. 428), and the note under Table I of Part II (p. 419). The letter-symbols here used are defined in the following Tables.

TABLE II.

Fluorescence Spectrum of Hexadeuterobenzene. Key to Assignments (cf. Table I).

	Freq. (cm.$^{-1}$).	p'.	p''.	s.
A	= 38290 + 499 + 879p' − 943p'' − 141s	0, 1	0—4	0—3
B	= ,, − 579 + 879p' − 943p'' − 141s	0, 1	0—5	0—5
C	= ,, + 2 × 499 − 579 − 943p'' − 141s		0—3	0—3
D	= ,, + 499 − 2 × 579 − 943p'' − 141s		0—2	0—3
E	= ,, + 499 − 2 × 496			
F	= ,, − 579 − 2 × 496 − 943p''		0, 1	
G	= ,, − 579 + 2 × 382			
H	= ,, − 579 + 2 × 208 − 141s			0, 1
I	= ,, − 579 − 2 × 350			
J	= ,, − 141s			1—3
K	= ,, + 499 − 114 − 943p'' − 141s		0, 1	0, 1
L	= ,, − 579 − 114 − 943p'' − 141s		0—2	0, 1
M	= ,, + 499 − 208 − 141s			0—2
N	= ,, − 579 − 208 − 943p'' − 141s		0—4	0—2
O	= ,, − 208 − 141s			0, 1
P	= ,, − 579 − 2 × 662			
P′	= ,, − 2 × 662			
P″	= ,, − 579 + 2 × 454			
Q	= ,, − 2275 − 943p'' − 141s		0—2	0, 1
R	= ,, + 499 − 295 − 141s			0, 1
S	= ,, − 579 − 295 − 943p'' − 141s		0—4	0—3
T	= ,, − 579 + 2 × 306			
U	= ,, + 499 − 165			
V	= ,, − 579 − 165			
W	= ,, − 662 − 828 − 943p''		0—3	
X	= ,, − 2275 + 499 − 579 − 943p''		0, 1	
Y	= ,, + 499 − 2286 − 943p'' − 141s		0, 1	0, 1
Z	= ,, − 579 − 2286 − 943p''		0, 1	

TABLE III.

Fluorescence Spectrum of Hexadeuterobenzene. Assignment to Vibrations of the Vibration Frequencies (cm.$^{-1}$) contained in Table II.

Upper-state fundamental frequencies (+).	Lower-state fundamental frequencies (−).	Diffs. of upper- and lower-state fundamentals (−).	Vibration.
879	943	64	A_{1g}(C)
—	2286	—	A_{1g}(H)
382	496	114	A_{2u}(H)
306	—	295	B_{2g}(C)
—	828	165	B_{2g}(H)
499	579	80	E_g^+(C 1)
—	2275	—	E_g^+(H 1)
208	350	141	E_u^+(C)
454	662	208	E_g^-(H)

(2) *Band Series* A—D.—These four series control the general pattern of the spectrum (cf. Part I, Section 4). They confirm the already given frequencies of the electronic origin, and of the fundamental vibrations, E_g^+(C 1) and A_{1g}(C), in both the upper and lower electronic states (Part IV, Section 2).

The fluorescence spectrum of hexadeuterobenzene does not show the striking resonance effects which in the fluorescence spectrum of benzene arise from the almost exact degeneracy of the combination E_g^+(C 1) + A_{1g}(C) with the fundamental frequency E_g^+(C 2) in the electronic ground state of benzene. In the ground state of hexadeuterobenzene, the combination has the frequency 1522 cm.$^{-1}$, whilst the fundamental frequency, as we know from the Raman spectrum, is 1552 cm.$^{-1}$; and in the fluorescence spectrum, as in the Raman spectrum, one finds no obvious transfer of intensity due to resonance between these two energy levels. Indeed, in the fluorescence spectrum, we can see nothing of the band which could arise from a transition between the " vibrationless " upper state and the E_g^+(C 2) fundamental level of the lower electronic state. The position is over-lapped by the tail of the combination band situated 1522 cm.$^{-1}$ below the electronic origin, but a band 1552 cm.$^{-1}$ from the origin, unless it were quite weak, should be visible as a disturbance to the rotational envelope.

(3) *Band Series* H, I, *and* J.—These series depend on changes of two or zero in the quantum number of the low-frequency vibration, E_u^+(C). They contribute, along with similar series in the absorption spectrum of hexadeuterobenzene, to the determination of the lower- and upper-state fundamental frequencies of this vibration, *viz.*, 350 cm.$^{-1}$ and 208 cm.$^{-1}$, as already noted in Part IV, Section 3.

Series H consists of a negatively running sequence in 141 cm.$^{-1}$, which starts with a band H_0^0 situated 415 cm.$^{-1}$ above B_0^0. In this sequence we are observing downward 2—0, 3—1, . . . , transitions of the E_u^+(C) vibration, in combination with those electronic and vibrational transitions which, when alone, produce the active origin B_0^0. These bands provide a value for the upper-state overtone frequency of the vibration E_u^+(C).

The band I_0^0, lying 704 cm.$^{-1}$ below B_0^0, arises from a downward 0—2 transition of the vibration E_u^+(C), combined in the same way with the electronic and vibrational transitions characteristic of B_0^0. This band gives us a value for the lower-state overtone frequency. Because of the degenerate character of the vibration, and its not particularly small Boltzmann factors, the transitions 2—0 and 0—2 might also be expected to appear without an accompanying change in any other vibration (Part I, Section 5). But the bands which could thus arise cannot be verified because of overlapping.

The transitions 1—1, 2—2, . . . , of the vibration E_u^+(C) occur as the sequences in 141 cm.$^{-1}$ which are found in most of the stronger series of the fluorescence, as of the absorption, spectrum of hexadeuterobenzene. But the degenerate nature of the vibration also permits transitions 1—1, 2—2, . . . , without accompanying changes in other vibrations (*loc. cit.*). Such transitions form the bands of series J, which are prominent in the fluorescence, as well as in the absorption, spectrum of hexadeuterobenzene (cf. Part IV, Section 3). The series consists essentially of a negative sequence in 141 cm.$^{-1}$, which runs as if from the forbidden electronic origin, except that the 0—0 band is missing.

(4) *Band Series* E, F, G, K, *and* L.—For reasons given in Part XI we assign the vibration frequencies peculiar to these bands to the hexagonal, out-of-plane vibration A_{2u}(H). Certain series related to this vibration were also found in the absorption spectrum of hexadeuterobenzene (Part IV, Section 5). However, the fluorescence spectrum of hexadeuterobenzene supplies more complete evidence concerning the fundamental frequencies of this vibration than can be obtained from the absorption spectrum. In different series of the fluorescence spectrum we find the upper-state overtone frequency, the lower-state overtone frequency, and the difference between the fundamental frequencies in the two electronic states, all agreeing with the deduced fundamental frequencies of the vibration, 496 cm.$^{-1}$ and 382 cm.$^{-1}$, in the lower and upper states, respectively.

The series E and F start with bands E_0^0 and F_0^0, situated 993 cm.$^{-1}$ below A_0^0 and B_0^0, respectively. Evidently they involve the excitation of two quanta of this vibration in the lower electronic state, in combination with those electronic and vibrational changes which by themselves produce the bands of series A and B respectively. These bands provide a value, 993 cm.$^{-1}$, for the lower-state overtone frequency. They are rather stronger than overtone bands usually are. In the Raman spectrum of hexadeuterobenzene the overtone of the A_{2u}(H) vibration appears more strongly than is usual for first overtones, and much more strongly than does the corresponding overtone in the Raman spectrum of benzene. We explain this by assuming for hexadeuterobenzene a certain amount of intensification of the overtone frequency, 2×496 cm.$^{-1}$, by resonance with the very strong A_{1g}(C) frequency at 943 cm.$^{-1}$, even though the separation of the two amounts to 50 cm.$^{-1}$. Similarly we suppose that the E and F bands of the fluorescence spectrum owe their relative prominence to resonance with those bands of the A_{1g}(C) progressions of series A and B, which lie 50 cm.$^{-1}$ below them.

The weak band G_0^0, situated 765 cm.$^{-1}$ above B_0^0, is assumed to involve a transition from the second quantum level of the A_{2u}(H) vibration in the upper electronic state, the loss of both quanta being superposed on those electronic and vibrational changes which characterise the strong origin B_0^0. This band furnishes a value, 765 cm.$^{-1}$, for the upper-state overtone frequency.

The series K and L, like the identically named series of the absorption spectrum (cf. Part IV, Section 5), consist of a number of bands of moderate intensity, negatively displaced by 114 cm.$^{-1}$ from the more prominent bands of series A and B respectively. They arise from 1—1 transitions of the A_{2u}(H) vibration, in combination with those electronic and vibrational transitions which produce the related A and B bands. The sequence interval, 114 cm.$^{-1}$, corresponds to the difference between the fundamental frequencies of the vibration A_{2u}(H) in the lower and upper electronic states.

(5) *Band Series* M, N, O, P, P′, *and* P″.—If we accept the assignments given in Part XI, all these bands are connected in one way or another with the degenerate, out-of-plane vibration, E_g^-(H). Again the fluorescence spectrum of hexadeuterobenzene provides more complete evidence concerning the fundamental frequencies of this vibration than can be obtained from the absorption spectrum (Part IV, Section 6), since in fluorescence we find the upper- and lower-state overtone frequencies, as well as the difference between the fundamental frequencies in the two states, all agreeing with the deduced fundamental frequencies, 662 cm.$^{-1}$ and 454 cm.$^{-1}$, for the lower and upper states, respectively.

Series M and N, like the identically named series of the absorption spectrum (Part IV, Section 6), consist of a number of bands of moderate intensity negatively displaced by 208 cm.$^{-1}$ from bands of series A and B, respectively. They arise from 1—1 transitions of the vibration E_g^-(H), superposed on those electronic and vibrational changes which produce the related A or B bands. The interval 208 cm.$^{-1}$ corresponds to the difference between the fundamental frequencies of the vibration in the two electronic states.

The degeneracy of the vibration permits a 1—1 transition in combination with the electronic transition only, and without other vibrational changes (Part I, Section 5). Thus arises the band O_0^0, which appears 208 cm.$^{-1}$ below the forbidden electronic origin. It is the parent band of the series O, which consists of a negatively-running sequence in the interval, 141 cm.$^{-1}$, n—n transitions in the vibration E_u^+(C) being here combined with 1—1 transitions of the vibration E_g^+(H). The same series, containing identically the same bands, is observed in the absorption spectrum (Part IV, Section 6).

The bands P and P′ lie 1332 cm.$^{-1}$ below the active origin B_0^0, and the electronic origin J_0^0, respectively. In explanation of them, we assume an excitation of the first overtone of the vibration E_g^-(H) in the lower electronic state, the interval, 1332 cm.$^{-1}$, representing the overtone frequency. Band P involves a combination of the overtone excitation with the electronic and vibrational transition characteristic of the strong fluorescence origin B_0^0. Band P′ involves no vibrational change other than the overtone excitation, this transition being made possible by the degenerate nature of the vibration E_g^-(H) (Part I, Section 5).

A very weak band P″ is situated 907 cm.$^{-1}$ above the main fluorescence origin B_0^0. We assume a prior excitation of the E_g^-(H) vibration by two quanta in the electronically excited state, the transition involving the loss of these quanta in combination with those electronic and vibrational changes which alone would produce the origin B_0^0. This band furnishes a value, 907 cm.$^{-1}$, for the upper-state overtone frequency of the vibration E_g^-(H).

(6) *Band Series* Q, X, Y, *and* Z.—These series all involve the excitation in the lower electronic state of one of the hydrogen-stretching frequencies—either E_g^+(H 1) or A_{1g}(H).

The progression and sequences which constitute series Q start with a band Q_0^0 lying 2275 cm.$^{-1}$ below the electronic origin. In explanation we assume a transition from the "vibrationless" level of the electronically excited state to the fundamental level of the degenerate vibration E_g^+(H 1) in the electronic ground state. As with the corresponding series in the fluorescence spectrum of benzene (cf. Part III, Section 5), the E_g^+(H 1) vibration here appears with a fundamental frequency, 2275 cm.$^{-1}$, which is 0·4% greater than the frequency, 2264·9 cm.$^{-1}$, observed in the Raman spectrum of liquid hexadeuterobenzene (Poole, *J.*, 1946, 252). We suggest a similar explanation, *viz.*, that, in the Raman spectrum of the liquid, the frequency is reduced by an interaction, which becomes permitted in the presence of cohesive forces, with the slightly higher, but close-lying and intense, fundamental frequency A_{1g}(H).

The two strongest bands of series Q have weak companions, negatively displaced by 80 cm.$^{-1}$: they constitute series X. The displacement corresponds to the difference between the fundamental frequencies of the vibration E_g^+(C 1) in the lower and upper electronic states, and we therefore assume the bands of series X to involve 1—1 transitions of this vibration, superposed on those transitions which produce the associated bands of series Q. Thus series X is related to series Q, exactly as series C is to series A, or as series D is to series B.

The parent bands, Y_0^0 and Z_0^0, of the somewhat weak series Y and Z are found 2286 cm.$^{-1}$ below the active orgins A_0^0 and B_0^0, respectively. We assume these series to arise in an excitation, in the electronic ground state, of one quantum of the totally symmetrical, hydrogen-stretching vibration, A_1(H), this excitation being superposed on those electronic and vibrational changes which produce the bands of series A and B respectively. The fundamental frequency of the vibration A_{1g}(H), as given by the displacement of Y_0^0 from A_0^0, or of Z_0^0 from B_0^0, is 2286 cm.$^{-1}$. The value given by the Raman spectrum of liquid hexadeuterobenzene is 2292·6 cm.$^{-1}$ (Poole, *loc. cit.*). The difference may not be significant, but if it is, it can be explained on the lines suggested above.

(7) *Band Series* R, S, *and* T.—According to our assignment, which we seek to justify in Part XI, the special vibrational changes which characterise these bands are related to the trigonal, out-of-plane vibration, B_{2g}(C). Closely related series are found in the absorption spectrum of hexadeuterobenzene. Together, these series provide values for the fundamental frequencies, 602 cm.$^{-1}$ and 307 cm.$^{-1}$, of the vibration B_{2g}(C) in the two electronic states (cf. Part IV, Section 8).

Series R and S, like the identically named series of the absorption spectrum, consist of bands of moderate intensity negatively displaced by 295 cm.$^{-1}$ from the stronger bands of series A and B, respectively. We interpret the interval 295 cm.$^{-1}$ as the difference between the two fundamental frequencies of the vibration B_{2g}(C). The bands arise when 1—1 transitions of this vibration become combined with those electronic or vibrational changes which, if alone, would produce the associated bands of series A and B.

The band T_0^0 is situated 613 cm.$^{-1}$ above the main fluorescence origin B_0^0. It is assumed to involve the prior excitation of the first overtone frequency of the vibration B_{2g}(C) in the upper electronic state: the transition involves the loss of these two quanta, in association with those electronic and vibrational changes which characterise B_0^0. A band, also called T_0^0, lying 613 cm.$^{-1}$ above the main absorption origin A_0^0, is found in the absorption spectrum of hexadeuterobenzene (cf. Part IV, Section 8); and it is given a similar explanation. The common interval, 613 cm.$^{-1}$, is taken as the upper-state overtone frequency.

(8) *Band Series* U, V, *and* W.—In Part XI we give reasons for connecting these bands with excitations, in either or both of the interacting states, of the trigonal, out-of-plane vibration, B_{2g}(H). Some related series are found in the absorption spectrum of hexadeuterobenzene. Together, the absorption and fluorescence series furnish values for the two fundamental frequencies, 828 cm.$^{-1}$ and 663 cm.$^{-1}$, of the B_{2g}(H) vibration (cf. Part IV, Section 9).

The weak series U and V correspond closely to the similarly named series of the absorption spectrum. In fluorescence, each is represented by a single listed band, though several further V bands can be seen on the plates. In absorption and fluorescence, the common characteristic of U and V bands is that each is negatively displaced by 165 cm.$^{-1}$ from an A or B band. The interval is interpreted as the difference between the fundamental frequencies of the vibration B_{2g}(H) in the lower and upper electronic states. In the formation of U and V bands, a 1—1 transition of this vibration accompanies those electronic or vibrational changes which, when alone, produce the associated A or B bands.

The progression W starts with a band 1490 cm.$^{-1}$ above the electronic origin. We assign this interval as the frequency of a combination between two vibrations in the electronic ground state: E_g^-(H)662 + B_{2g}(H)828 = 1490 cm.$^{-1}$. The combination has the symmetry E_g^+, and therefore could constitute the terminal vibrational level of a transition from the "vibrationless" excited state (Part I, Section 5). On the other hand, this particular combination frequency has not been observed in the Raman spectrum, and therefore one naturally looks for some special explanation of the relative strength and persistence of the W progression in the fluorescence spectrum. Our explanation assumes an intensification by resonance with bands of the B progression. Each W band lies only about 30 cm.$^{-1}$ away from a strong B band, and each of these close pairs of bands fulfils the conditions for resonance.

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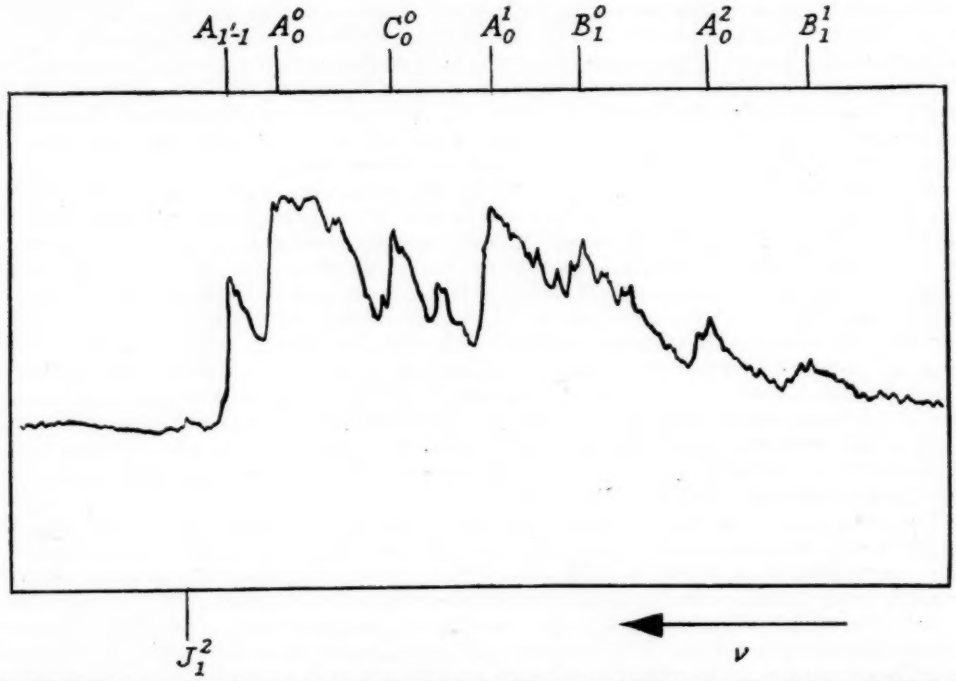
100. *Excited States of Benzene. Part VI. Description and Analysis of the First Ultraviolet Band System of the Absorption Spectrum of* 1 : 3 : 5-*Trideuterobenzene.*

By FRANCESCA M. GARFORTH, CHRISTOPHER K. INGOLD, and HARRY G. POOLE.

The ultraviolet absorption spectrum of 1 : 3 : 5-trideuterobenzene is described, and measurements of the frequencies of many bands are recorded. A complete vibrational analysis of the spectrum is given. The partial loss of symmetry arising from the isotopic loading of this molecule modifies, and thus confers spectral activity on, vibrations which did not involve themselves with the electronic transitions of benzene and hexadeuterobenzene. Fourteen fundamental frequencies of the upper electronic state, and six of the lower state, are recognised, and all are assigned to their vibrations. Part of the theoretical basis of these assignments is reserved for treatment in Part XI.

(1) *Measurements.*—The 1 : 3 : 5-trideuterobenzene was prepared by deuteration of aniline and subsequent deamination (Best and Wilson, *J.*, 1946, 239). Its purity was established by isotopic analysis, and by the already reported work on its infra-red and Raman spectra (Bailey, Poole, and others, *J.*, 1946, 255). It was transferred to the absorption assembly by sublimation at a low pressure from the cooled solid. The assembly, pumped to 10^{-3} mm. with the trideuterobenzene at liquid-air temperature, consisted of a quartz tube, 50 cm. long and 2·5 cm. diameter, with sealed-in end-windows, and a side-tube giving connexion, through a quartz-to-Pyrex graded seal, with a Pyrex bulb containing the liquid or solid sample. In operation, the controlled temperature of this bulb determined the pressure in the absorption tube. The temperatures employed varied from − 50° to + 20°, the corresponding pressures ranging from less than 1 mm. to about 74 mm.

FIG. 1.



Microphotometer record of part of the first strong period in the absorption system of 1 : 3 : 5-*trideuterobenzene. The spectrum is shown from about* 38800 *cm.*$^{-1}$ *to about* 38300 *cm.*$^{-1}$. *In this record the conditions were chosen for exhibiting medium bands, such as* $A_{1'-1}$. *For this reason the upper part of the band* A_0^0 *has become truncated: this band is really much stronger, relatively to the other bands, than would appear from this photograph.*

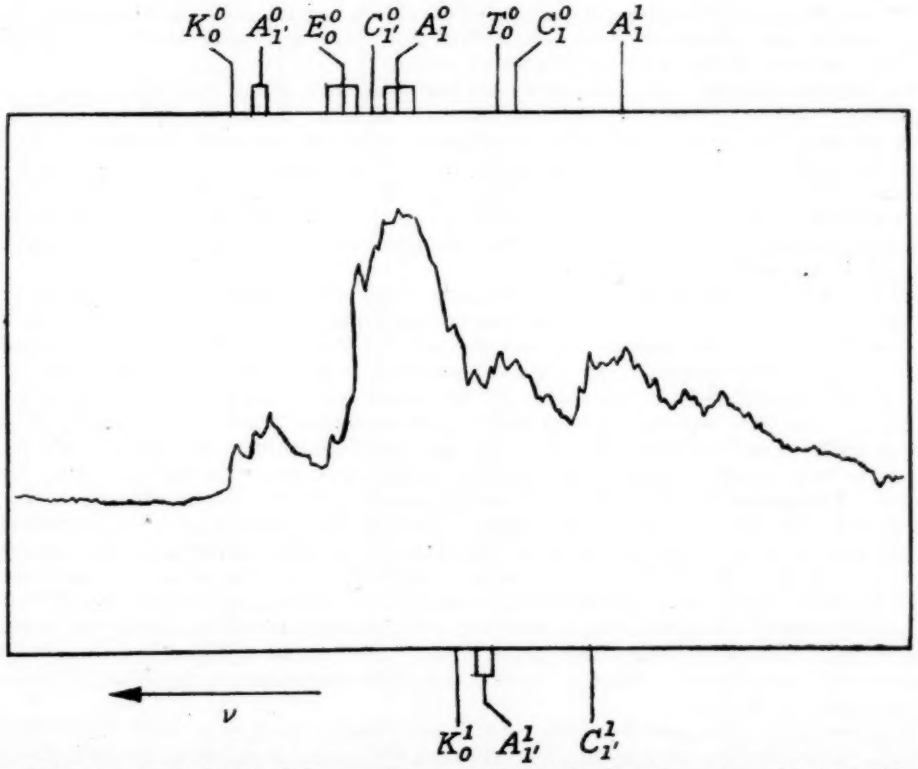
(*The original microphotometer record had to be rephotographed and intensified several times in order to obtain a tracing thick enough for the preparation of a block. The fine line on the original record resolves the closely overlaid bands considerably more completely than does the reproduction.*)

The light-source was a water-cooled, hydrogen-discharge tube. The spectrograph, Hilger's quartz, Littrow-pattern instrument of 170 cm. focal length, was kept in a thermostatted room at 20·0°. Its dispersion, in the region 2700—2200 A., in which it was focused for these experiments, was about 3 A./mm., or about 48 cm.$^{-1}$/mm. at 2500 A. The slit-width was adjusted to 0·02 mm. The spectra were recorded on 25 cm. × 10 cm., Kodak, L15 plates, which were developed for 3·0 mins. at 18°, fixed in a hardening-fixing bath, washed, and dried in dust-free air. The iron-arc was used to provide a comparison spectrum, which was recorded just above and just below the absorption spectrum, without disturbing the plate, with the aid of a suitably perforated Hartmann diaphragm.

Direct measurement of the bands by means of the travelling microscope was, on the whole, not satisfactory, though in favourable cases a setting could be reproduced to 0·01 mm. The usual difficulty, however, was to set the microscope accurately to the intensity maxima of any but sharp and well-isolated bands, the eye being but a poor judge of intensity variation in complex

band-groups. For this reason we have preferred to evaluate the spectra in the form of microphotometer records, taken with the aid of a Zeiss recording microphotometer. Each spectrogram was thus reproduced, at a dispersion of about 6 cm.$^{-1}$/mm., in a series of records of total length 120—150 cm. For the evaluation of records, the methods described by Poole (*J.*, 1946, 248) were assisted, in the present experiments, by over-printing, on each microphotometer record of the absorption spectrum, a record of the associated iron-arc spectrum, this being done without disturbance either to the plate or to the record-holder by adjusting, between exposures, the diaphragm which limits the effective length of the microphotometer slit. The width of the microphotometer slit was adjusted to 0·03 mm. : spectral features 1 cm.$^{-1}$ apart could then be resolved, whilst the maxima of the sharper bands could be located to within this limit.

FIG. 2.



Microphotometer record of part of the second strong period in the absorption system of 1 : 3 : 5-*trideuterobenzene. The spectrum is shown from about* 39800 cm.$^{-1}$ *to about* 39300 cm.$^{-1}$. *The conditions are chosen to show strong bands, with the result that weak ones cannot, or can scarcely, be seen. The band* A_0^0 *of the first strong period becomes replaced in this period by the whole group from* K_0^0 *to* A_1^0. *In later periods the complexity grows until the contour appears almost continuous.*

(*See remark in parenthesis under Fig.* 1.)

Qualitatively, the general structure of the spectrum is the same as that of the absorption spectrum of benzene or of hexadeuterobenzene (cf. Part I, Section 4, and Fig. 1, p. 409), except for one very obvious difference, *viz.*, that, as the progressions run out towards shorter waves, the sequence pattern, instead of being rather closely repeated, becomes rapidly more complicated, until after four or five repetitions the now very numerous overlapped bands become blurred into a continuous contour—in which, at best, the main components only can be very roughly located. Thus we can observe the spectrum over a considerably greater frequency range than that over which we can make measurements of the bands. This stage-wise development of practical continuity, the first step of which is illustrated by a comparison of Figs. 1 and 2, shows clearly how an apparently continuous spectrum can arise from a polyatomic molecule, not necessarily because of any dissociation or pre-dissociation, but simply from the number and

variety of the allowed vibrational transitions. We explain the present somewhat rapid development of complexity along the spectrum on the ground that, in this D_{3h} benzene, not one but two totally symmetrical carbon vibrations can undergo quantum changes without symmetry restriction and with comparable probabilities, so that, in the upper electronic state, one totally symmetrical quantum can be excited in two ways, two in three ways, and so on.

Each of the stronger bands of the totally symmetrical progressions is the parent of a sequence due to n—n transitions of the degenerate, low-frequency vibration, and the successive bands of the sequence show increasing complexity. This phenomenon was also apparent in the absorption spectra of benzene and hexadeuterobenzene. We explain it on the ground (Part II, Section 1) that when in either electronic state several degenerate quanta are excited, anharmonicity splits up the higher-order degeneracies which would otherwise characterise the combination. Thus two degenerate quanta give three, not exactly coincident, energy levels, and therefore a triple band if the other combining level is single, and the selection rules allow all three combinations. More complex band groups can arise when several degenerate quanta are involved in either, or, still more, in both, of the combining electronic states.

Two special causes of band complexity are best illustrated in the individual cases in which they arise. One is the exchange of a lower-state quantum for an upper-state quantum of nearly the same frequency. The other is resonance, which causes bands that might have been invisible to appear more or less strongly on the flanks of strong bands. Superposed on all these effects is that of molecular rotation, a quite general cause of discrete band structure. Even the simplest bands exhibit a more or less distinct structure, overlying that general degradation of intensity towards the red which shows that the molecule becomes slightly expanded in the upper electronic state.

We have found band complexity of some value as a guide to assignment. When, for instance, in a smoothed and nearly featureless region of the spectrum, a single sharp band (such as Y_0'—see Section 8) stands out, one can feel sure that it is simply constituted, involving few excited quanta, and probably no more than one degenerate quantum in either electronic state.

Our measurements of the frequencies of the bands are in Table I. Each region of the spectrum was studied with the aid of at least 4, and sometimes 7, independent plates, of which 20 were taken in all. Where a decimal is quoted, the frequencies, corrected to vacuum, are believed to be accurate to within 1 cm.$^{-1}$, whilst in other cases errors of a few wave-numbers are possible. The qualitative indications of intensity (ranging from ew = extremely weak, through m = medium, etc., to vs = very strong) relate to absorption in a 50-cm. column of vapour at the saturation pressure corresponding to the temperature stated: the pressure at 0° is computed to be 27 mm., and, at − 35°, rather less than 3 mm. We do not record the weakest of the measured extremely weak bands, since we believe that some at least of them are only accidental concentrations of intensity in a continuous background, presumably composed of overlapped bands too numerous and too weak for separate observation. The symbol δ, applying to the last four entries of the Table, means "diffuse": in these cases the uncertainty in the recorded frequency is of the order of 10 cm.$^{-1}$.

Assignments are expressed by means of a literal notation the key to which is in Tables II and III. The subscripts and superscripts represent the quantum numbers, in either electronic state, of the A_1'(C), A_1'(C′), and E''(C) vibrations, as explained in the Note below Table I. The letter-symbols distinguish those vibrational changes which are peculiar to the different band-series, and are defined by the equations of Table II, which also gives the observed ranges of the above-mentioned quantum numbers. Identification of the vibrations symbolised in Table III will be assisted by reference to Part I, Section 6, especially to Table III in that Section (p. 413) (for diagrams, see *J.*, 1946, pp. 260—271).

The band-series A—E, G, H, J, M, and N correspond as closely as the different symmetries of the molecules allow to the identically named series in the absorption spectra of benzene and hexadeuterobenzene (Parts II and IV).

(2) *Band Series* A—D *and* E, e.—As with the D_{6h} benzenes, so with the D_{3h} benzene, the bands of series A—D constitute the main framework of the absorption spectrum (cf. Part I, Section 4). They are dependent on unit quantum changes in the planar, carbon-bending vibration E'(C 1), which directly produce the four origins, A, B, C, and D. Progressions in the two trigonal ring-swelling vibrations, A_1'(C) and A_1'(C′), are, of course, mainly positive, although several one-quantum members of the corresponding negative progressions can be seen, much weakened by their Boltzmann factors. In all these progressions both the totally symmetrical carbon vibrations are involved, that with the lower frequency in either state giving stronger bands than the other (see Figs 1 and 2). Thus the one-quantum member of the positive A progression is

TABLE I.

Absorption Spectrum of 1 : 3 : 5-*Trideuterobenzene. Frequencies, Intensities, and Assignments* (*cf. Tables II and III*).

Freq. (cm.$^{-1}$).	Inty. (0°).	Assgnt.	Freq. (cm.$^{-1}$).	Inty. (−35°).	Assgnt.	Freq. (cm.$^{-1}$).	Inty. (−35°).	Assgnt.
36586	ew	B^0_{-1}	38432·0	ew	$B^1_{1'}$, L^1_0	39465	mw	$B_{1+1'}$
638	vw	B^0_{-1}	450·8	vw	s^0_1	472·8	vw	E^1_0
37135	vw	B^3_0	456·3	vw		485·8	mw	L^0_1
146	vw		466	w	C^1_0	498·8	vw	C^0_1
206	vw	D^2_0	470	w		507·7	m	
225	vw	N^1_0	481·8	ms	B^0_1, M^0_0	518·3	m	T^0_0
296·1	mw	B^2_0	490·7	vw		523·7	vw	$A^1_{1'}$
347·5	vw	D^1_0	500·3	w	$D^0_{1'}$	535·5	w	K^1_0
358·2	w		515	w	r^1_0	547·8	w	
368·7	vw	N^0_0	545·9	s	A^1_0	575·2	vs	A^0_1
379·8	w		551·3	vw		585·4	vs	
386	ew	v^0_0	580·5	mw	$B^0_{1'}$	595	vs	
391	w		584·9	mw	L^0_0	601	s	$C^0_{1'}$
402·7	vw	s^1_0	615·2	m	C^0_0	610·6	s	E^0_0
408·0	vw		669·5	ms	r^0_0	618·5	w	
445·0	ms	B^1_0	685·8	vs	A^0_0	630·5	ms	
472·0	w	U^0_0	693·5	vs		670·9	s	$A^0_{1'}$
510·1	m	D^0_0	697·0	vs		681·3	s	K^0_0
523	w	B^0_{1-1}	729·3	m	$A_{1'-1}$	694·5	s	
558·8	m	s^0_0	760·1	w	J^2_1	745·3	ew	G^2_1
590·0	s	B^0_0	772·9	vw		808·8	ew	J^1_3
634·9	m	T′	836·5	vw	G^2_0	840·6	ew	$G^2_{1'}$
658·4	w	C^0_{-1}	847·7	vw		894	vw	G^1_1
692·0	mw	$A^0_{-1'}$	860·0	vw	F^1_0	901	w	F^0_1
732·9	mw	J^3_0	923	w	$J^1_{1'}$	911	vw	R^1_0
740·0	m	A^0_{-1}	954	vw	S^0_0	982·6	vw	$G^1_{1'}$
774	vw	$A^0_{1'-2}$	988·3	mw	G^1_0	40020	mw	G^0_1
805·8	vw	j^2_0	996·2	w		037	mw	
820·6	vw	Q^1_0	39008·0	w	F^0_0	048·7	mw	R^0_0
879	mw	J^2_0	019·9	vw	$J^1_{1'}$	052·9	mw	
889	mw	H^1_0	062	w	B^2_2	060	mw	
937	w	I^0_0	138	vw	G^0_0	078	ew	l_1
957·4	w	j^1_0	144·0	ms		116·9	w	$G^0_{1'}$
970	w	Q^0_0	149	w	D^1_2	127	w	
985	w	l′	163	vw	P^0_0	250	mw	B^0_3
38032	m	J^1_0	177	w		280·3	mw	$A^2_{1+1'}$
039·9	m	H^0_0	191·9	vw	l_0	316	mw	W^0_1
122·6	mw	N^1_1	203	w	C^2_1	330·1	m	A^1_3
	Inty. (−35°)		218·7	w	B^1_2, M^1_1	340·5	m	
169	vw	B^2_1	243	vw	O^1_0	348	m	$C^1_{1+1'}$
177	w		272·3	vw	W^1_0	357·9	m	E^1_1
208	ew	U^1_1	280·1	w	A^2_1	369·8	m	
233·8	vw	A^3_0	295	w	D^0_2	403·1	mw	C^0_2
240·9	vw		305·5	w	$C^2_{1'}$	413	mw	T^0_1
255·1	vw	D^1_1	350·2	w	C^1_1	421·4	mw	$A^1_{1+1'}$
274·7	vw	N^0_1	368·1	ms	B^0_2, M^0_1	431·3	mw	
324·9	w	C^0_0	394·0	m	O^0_0	471	ms	A^0_2
331·4	w	B^1_1, M^1_0	406	vw	W^0_0	478	s	
341·9	ew	$D^1_{1'}$	413·1	w		483	ms	
361·9	w	U^0_1	431·4	s	A^1_1	490·2	s	$C^0_{1+1'}$
394·5	mw	A^2_0	441	s		505·8	ms	E^0_1
403	w	D^0_1	449·6	s		520	ms	
			458	s	$C^1_{1'}$			

TABLE I—*contd.*

Freq. (cm.$^{-1}$).	Inty. (−35°).	Assgnt.	Freq. (cm.$^{-1}$).	Inty. (−35°).	Assgnt.	Freq. (cm.$^{-1}$).	Inty. (−35°).	Assgnt.
40573·7	ms	$A^0_{1+1'}$, K^0_1	41028	w	y^0_0	41449·6	m	A^0_{2+1}, K^0_2
580·7	ms		086	w	$C^2_{2+1'}$	458·5	m	
587·4	ms		163	mw	$A^2_{2+1'}$	479·9	mw	
603·9	m	$E^0_{1'}$	227·0	mw	A^1_3	510	vw	$E^0_{1+1'}$
617·4	vw		235·0	m	$C^1_{2+1'}$	547·2	vw	e^0_0
651·0	w	$A^0_{2'}$, $K^0_{1'}$	246	w	E^1_2	565	vw	$A^0_{1+2'}$
663·2	m		259	mw		830·4	m	$Y^0_{0'}$
670·1	w		270	m	$X_0{}'$	875	w	Y^0_1
920	mw	G^0_2	306·5	mw	T^0_2	~42130	w(δ)	A^1_4
933	mw		319·1	mw	$A^1_{2+1'}$	168	w	$X^{-\prime}$
945	mw	R^0_1	371	ms	A^0_3	~42260	m(δ)	A^0_4, E^0_3
996	mw	Y^0_0	386	ms	$C^0_{2+1'}$	~42290		
41012	w	$G^0_{1+1'}$	396	ms	E^0_2	~42350	mw(δ)	$A^0_{3+1'}$
019·8	w							

Note: In the assignment column, the upper-state quantum numbers, called p' and q' in Table II, are given as subscripts with (stated or implied) positive signs, and the lower-state numbers, p'' and q'' in Table II, as subscripts with negative signs. These mark progressions in the totally symmetrical vibrations A_1'(C) and A_1'(C'), p' and p'' referring to the former, and q' and q'' to the latter. The absence of a dash upon a subscript means that it refers to the totally symmetrical vibration, A_1'(C), of lower frequency, and therefore to p' or p''; whilst a subscript with a dash relates to the totally symmetrical vibration of higher frequency, A_1'(C'), and thus to its quantum number q' or q''. The quantum number s of Table II, which is common to both the upper and lower electronic states, is given in the assignment column as a superscript. It marks sequences in the low-frequency vibration E''(C). With regard to the naming of the vibrations, see Part I, Section 6.

TABLE II.

Absorption Spectrum of 1 : 3 : 5-*Trideuterobenzene. Key to Assignments* (*cf. Table I*).

	Freq. (cm.$^{-1}$).	p', p''.	q', q''.	s.
A =	38184 + 513{+ 893p' + 988q' − 956p'' − 1005q''} − 150s	0—4 / 0—2	0,1 / 0, 1	0—3
B =	" − 594{+ 893p' + 988q' − 956p'' − 1005q''} − 150s	0—3 / 0, 1	0, 1 / 0, 1	0—3
C =	" + 2 × 513 − 594{+ 893p' + 988q' − 956p''} − 150s	0—2 / 0, 1	0—2	0—2
D =	" + 513 − 2 × 594 + 893p' + 988q' − 150s	0—2	0, 1	0—2
E =	" + 1428 + 893p' + 988q' − 150s	0—3	0, 1	0, 1
e =	" + 513 + 2 × 1428			
F =	" + 824 + 893p' − 150s	0, 1		0, 1
G =	" + 513 + 2 × 223 + 893p' + 988q' − 150s	0—2	0, 1	0—2
H =	" − 594 + 2 × 223 − 150s			0, 1
I =	" + 513 − 2 × 373			
J =	" + 893p' + 988q' − 150s	0—2	0, 1	1—3
j =	" + 513 − 594 − 150s			1, 2
K =	" + 513 + 2 × 495 + 893p' − 150s	0—2		0, 1
L =	" − 594 + 2 × 495 + 893p' − 150s	0, 1		0, 1
l =	" + 513 + 495 + 893p'	0, 1		
l′ =	" + 513 − 710			
M =	" + 513 − 215 + 893p' − 150s	0, 1		0, 1
N =	" − 594 − 215 + 893p' − 150s	0, 1		0, 1
O =	" + 1428 − 215 − 150s			0, 1
P =	" + 2 × 495			
Q =	" − 215 − 150s			0, 1
R =	" + 513 + 2 × 680 + 893p' − 150s	0, 1		0, 1
r =	" + 513 + 680 − 710 − 150s			0, 1
S =	" − 594 + 2 × 680			
s =	" − 594 + 680 − 710 + 893p' − 150s	0, 1		0, 1
T =	" + 513 + 2 × 411 + 893p'	0—2		
T′ =	" + 513 − 2 × 531			
U =	" − 594 − 119 + 893p'	0, 1		0, 1
v =	" − 594 − 200			
W =	" + 513 + 2 × 360 + 893p' − 150s	0, 1		0, 1
X′ =	" + 3085 + 893p'	0, 1		
Y =	" + 513 + 2300 + 893p'	0, 1		
Y′ =	" + 513 + 3135			
y =	" + 513 + 2330			

Note: The frequency 38184 cm.$^{-1}$ is that of the forbidden electronic origin. The other frequencies are vibration frequencies. They are assigned in Table III.

TABLE III.

Absorption Spectrum of 1 : 3 : 5-*Trideuterobenzene. Assignment to Vibrations of the Vibration Frequencies (cm.*$^{-1}$*) contained in Table II.*

Upper-state fundamental frequencies (+).	Lower-state fundamental frequencies (−).	Diffs. of upper- and lower-state fundamentals (−).	Vibration.
893	956	67 } (+ 32)	A_1'(C)
988	1005	— }	A_1'(C′)
2300	—	—	A_1'(H)
3135	—	—	A_1'(H′)
360	—	—	A_2''(C)
411	531	119	A_2''(H 1)
—	—	200	A_2''(H 2)
513	594	81	E'(C 1)
1428	—	—	E'(C 2)
2330	—	—	E'(H 1)
3085	—	—	E'(H′ 1)
824	—	—	E'(H 2)
223	373	150	E''(C)
495	710	215 } (− 30)	E''(H 1)
680	—	— }	E''(H 2)

Note: Concerning the frequency 824 cm.$^{-1}$, see text (Section 3). A value 715 cm.$^{-1}$ for the upper-state fundamental frequency of vibration A_2''(H 2) follows from the known ground-state frequency (Section 7).

double (A_1^0 and $A_{1'}^0$), the lower frequency being the stronger, whilst the two-quantum member is triple (A_2^0, $A_{1+1'}^0$, $A_{2'}^0$), the lowest frequency being the strongest and the uppermost the weakest (cf. Part I, Section 6).

This pattern of progressions is overlapped by that of the E series. The parent band, E_0^0, lies between A_1^0 and $A_{1'}^0$ (see Fig. 2). The one-quantum member of this progression is again double, the stronger band, E_1^0, fitting in between A_2^0 and $A_{1+1'}^0$, and the weaker one, E_1, between $A_{1+1'}^0$ and $A_{2'}$. As with the D_{3h} benzenes, so also with the D_{3h} compound, the E series is dependent on a one-quantum excitation of the planar carbon-stretching vibration E'(C 2), and is considered to obtain much of its intensity by resonance with the A series (Part II, Section 3).

The whole of this pattern of progressions is overlapped by the corresponding C pattern, whilst the combined A-and-C pattern becomes repeated at lower frequencies in the similar B-and-D pattern. Finally, all the stronger bands of all these branching progressions start negatively-running sequences involving 1—1, 2—2, . . . , transitions of the degenerate, out-of-plane, carbon vibration, E''(C).

The above-mentioned series, together with analogous band-series in the fluorescence spectrum of 1 : 3 : 5-trideuterobenzene (Part VII, Section 2), allow us to fix the position of the electronic origin,

$$J_0^0 = 38184 \pm 1 \text{ cm.}^{-1}$$

as well as the following fundamental vibration frequencies :

$$E'(\text{C 1})_{\text{ground}} = 594 \text{ cm.}^{-1} \qquad E'(\text{C 1})_{\text{excited}} = 523 \text{ cm.}^{-1}$$
$$E'(\text{C 2})_{\text{excited}} = 1428 \text{ cm.}^{-1}$$
$$A_1'(\text{C})_{\text{ground}} = 956 \text{ cm.}^{-1} \qquad A_1'(\text{C})_{\text{excited}} = 893 \text{ cm.}^{-1}$$
$$A_1'(\text{C}')_{\text{ground}} = 1005 \text{ cm.}^{-1} \qquad A_1'(\text{C}')_{\text{excited}} = 988 \text{ cm.}^{-1}$$

and the following frequency difference :

$$E''(\text{C})_{\text{ground}} - E''(\text{C})_{\text{excited}} = 150 \text{ cm.}^{-1}$$

The ground-state frequencies, as found in the Raman spectrum of liquid 1 : 3 : 5-trideuterobenzene, are quoted for comparison : E'(C 1) = 593·0 cm.$^{-1}$, A_1'(C) = 956·2 cm.$^{-1}$, A_1'(C′) = 1003·6 cm.$^{-1}$ (Herzfeld, Ingold, and Poole, *J.*, 1946, 332).

The existence of two totally symmetrical vibrations of not very different frequencies, and of comparable activity for the development of progressions, leads to a phenomenon which is sufficiently uncommon to be notable, *viz.*, the appearance of satellite bands displaced from their principals by a small *positive* interval, in this case 32 cm.$^{-1}$. The bands $A_{1'-2}$ and $A_{1'-1}$ are examples of such satellites. The latter appears in Fig. 1 : it lies 32 cm.$^{-1}$ on the high-frequency

side of the very strong parent band A_0^0. Such satellites may be explained by an exchange of a ground-state quantum of the totally symmetrical vibration of lower frequency for an upper-state quantum of the totally symmetrical vibration with the higher frequency. In general such positive intervals may arise when both of the following conditions are fulfilled. The first is that two vibrations of the same symmetry class undergo such mutual modifications of normal co-ordinates in the altered electronic system that the presence of either vibration in the initial state tends to excite both in the final state. The totally symmetrical carbon vibrations of 1 : 3 : 5-trideuterobenzene constitute one such case; and the out-of-plane vibrations of partly deuterated benzenes in general provide other cases (cf. *J.*, 1946, 259, *et seq.*). The second condition is that the upper-state frequency of one such pair of vibrations lies above the lower-state frequency of the other. Intervals of this kind have been observed before by Ginsberg and Matsen in the absorption spectra of aniline and phenol (*J. Chem. Physics*, 1945, **13**, 167, 309).

The single band, called e_0^0, lying 2850 cm.$^{-1}$ above A_0^0, is attributed to the excitation, in the upper electronic state, of the first overtone of the stretching vibration E'(C 2), in association with those electronic and vibrational transitions which characterise the principal absorption origin A_0^0. The very appreciable intensity of this overtone band can be understood, since it falls among bands of the A progression, from which it could gain intensity by resonance.

(3) *Band Series* F.—The parent band, F_0^0, of series F is sharp, though somewhat weak. It lies 824 cm.$^{-1}$ above the electronic origin. We incline to the view that it is an individual band, and not an outlying component of the band G_0^1; but we have not been able fully to satisfy ourselves on this point. A similar difficulty arises in connexion with the other bands of the series. If these bands are indeed separate, then we can see no alternative to regarding them as involving the excitation in the upper electronic state of one quantum of the planar deuterium-bending vibration belonging to the E' symmetry class. The band F_0^0 would then arise in a transition from the " vibrationless " ground state to the fundamental level of this vibration in the upper electronic state.

The resulting vibration frequency,

$$E'(\mathrm{H}\ 2)_{\mathrm{excited}} = 824\ \mathrm{cm.}^{-1}$$

is only a very little smaller than the corresponding ground-state frequency, 833·5 cm^{-1}., as given in the Raman spectrum of liquid 1 : 3 : 5-trideuterobenzene (Herzfeld, Ingold, and Poole, *loc. cit.*). If we should look for a band depending analogously on an E' protium-bending frequency of the upper-state, assuming this frequency to lie somewhat near the corresponding lower state frequency (1101·8 cm.$^{-1}$, as given in the Raman spectrum) then we find several possible bands, all of which, however, are capable of alternative assignments. One naturally looks in the fluorescence spectrum for bands displaced by 833·5 and 1101·8 cm.$^{-1}$ below the electronic origin. Bands are indeed found in these positions, but, unfortunately, an alternative explanation is possible for each of them. In all the circumstances we regard our suggested assignment of the F series as provisional.

(4) *Band Series* G, H, I, J, *and* j.—All these series depend in special ways on the degenerate, low-frequency vibration, E''(C). Series G and H, which commence with bands, G_0^0 and H_0^0, lying 446 cm.$^{-1}$ above A_0^0 and B_0^0 respectively, involve the excitation, in the upper state, of two quanta of this vibration, in association with those electronic and vibrational transitions which characterise series A and B respectively. The sequences, in 150 cm.$^{-1}$, of series G and H therefore involve upward transitions of the type 0—2, 1—3, . . . , in the vibration E''(C).

The single weak band, I_0^0, situated 760 cm.$^{-1}$ below A_0^0, can be explained by assuming the loss of two ground-state quanta of the same vibration, in association with the transitions of A_0^0. The same band appears in the fluorescence spectrum, where it is the parent of a series (Part VII, Section 3). The resulting overtone-frequency is appreciably greater than twice the fundamental frequency, but this may be a real effect of anharmonicity, since we find a similar relationship in the Raman spectrum.

The degeneracy of the vibration, E''(C), would permit (Part I, Section 6) the excitation, in combination with the electronic transition, of its first overtone, without the need for accompanying excitations of other vibrations. In fact, an extremely weak band, situated 446 cm.$^{-1}$ above the electronic origin, has been observed, though we do not record it, since some equally faint intensity maxima have been rejected in case they should be spurious frequencies due to the overlapping of bands. The same symmetry conditions (*ibid.*) allow 1—1, 2—2, . . . , transitions of the vibration E''(C) to accompany the electronic transition, without simultaneous changes in

other non-totally symmetrical vibrations. Such transitions produce series J, a rather prominent series, closely similar to the identically named series of the D_{6h} benzenes. In the absorption spectrum of 1 : 3 : 5-trideuterobenzene, we find a negatively-running sequence in 150 cm.$^{-1}$, which starts as if from the electronic origin, except that the 0—0 band is absent. The same sequence is found in the fluorescence spectrum (Part VII, Section 3). In absorption the main bands of the sequence are also the starting points of positive progressions in the two totally symmetrical vibrations, A_1'(C) and A_1'(C').

Displaced below the bands of the J sequence by about 80 cm.$^{-1}$ lie the bands of a weak companion series, which we call j. It can be explained by assuming 1—1, 2—2, . . . , transitions of the vibration E''(C), superposed on 1—1 transitions of the vibration E'(C 1). These bands, too, are found in the fluorescence spectrum (*ibid.*). They are labelled j_0^1, j_0^2, . . . , and have two causes of spectral activity, *viz.*, the excitation of the vibrations E'(C 1) and E''(C), the latter being probably the more important. The series has a theoretical parent, j_0^0, in which the second vibration would be unexcited, the band arising from a pure 1—1 transition of the vibration E'(C 1). We might expect this band to be much weaker. In the absorption spectrum, the band can be seen, but is too weak to be included in our record. In the fluorescence spectrum the same band, though still very weak, can be measured satisfactorily: its frequency is 38105 cm.$^{-1}$ (Part VII, Table I).

These series furnish the following values for fundamental frequencies:

$$E''(\mathrm{C})_{\mathrm{ground}} = 373 \text{ cm.}^{-1} \qquad E''(\mathrm{C})_{\mathrm{excited}} = 223 \text{ cm.}^{-1}$$

The ground-state frequency, as measured in the Raman spectrum of liquid 1 : 3 : 5-trideuterobenzene is 372·7 cm.$^{-1}$ (Herzfeld, Ingold, and Poole, *loc. cit.*).

(5) *Band Series* K, L, l, l', M, N, O, P, *and* Q.—In Section 3 we did not quite fully describe the appearance of the branching progressions in the frequencies, 893 and 988 cm.$^{-1}$, of the two totally symmetrical vibrations, A_1'(C) and A_1'(C'). It has to be added that whenever an A_1'(C') quantum is present (as indicated by a dashed subscript in the band symbol), the corresponding band, if strong, is accompanied on its high-frequency side by a close companion of considerable strength. The companion bands to series A constitute series K (cf. Fig. 2), and those to series B form series L. Since the bands of series K and L are clearly gaining a great deal of their intensity by resonance with the neighbouring bands of series A and B, the upper-state vibration which is characteristic of series K and L must have total symmetry. There being no fundamental of an appropriate frequency, we take the vibration frequency to be that of a first overtone. The frequency is 996 cm.$^{-1}$, but this is probably raised a few wave-numbers by the resonance.

A single weak band P_0^0 lies 993 cm.$^{-1}$ above the electronic origin. We assign this band to the excitation in the upper electronic state of the same first overtone. The implication is that the corresponding fundamental vibration is degenerate, the overtone being here excited in its degenerate (E') form, not in its totally symmetrical (A_1') form (Part I, Sections 5 and 6).

With this same vibration we connect two series, M and N, which are prominent alike in the absorption and in the fluorescence spectrum (Part VII, Section 4). The bands of series M lie uniformly 215 cm.$^{-1}$ below bands of series A, whilst those of series N are displaced by the same amount below those of series B. The two series clearly correspond to the identically named series of the absorption and fluorescence spectra of benzene and of hexadeuterobenzene, though the common interval is 265 cm.$^{-1}$ for benzene, and 208 cm.$^{-1}$ for hexadeuterobenzene. We interpret the present series M and N in the same way as the others, *viz.*, as involving 1—1 transitions in some special vibration, in combination with those electronic and vibrational transitions which characterise series A and B, respectively. A weak series, called O, also occurs, the bands of which are displaced by 215 cm.$^{-1}$ below bands of series E. We assume the same 1—1 vibrational transition, now in combination with the electronic and vibrational transitions of series E.

A weak series called Q is present, which starts with a band, Q_0^0, situated 214 cm.$^{-1}$ below the electronic origin. A band in the same position is present in the fluorescence spectrum (Part VII, Section 4). In the production of these bands the 1—1 transition is unaccompanied by other vibrational changes, and this shows the vibration to be degenerate (Part I, Sections 5 and 6). Corresponding bands are found 265 cm.$^{-1}$ below the electronic origin in the absorption and fluorescence spectra of benzene, and 208 cm.$^{-1}$ below the origin in the corresponding spectra of hexadeuterobenzene.

The close analogy of series M, N, and Q with series of the D_{6h} benzenes requires us to assume

that the interval 215 cm.$^{-1}$, representing a difference of fundamental frequencies in the two electronic states, belongs to a vibration of the E'' class. Connecting it with the degenerate vibration whose overtone is concerned in series K, L, and P, we obtain agreement with the known ground-state frequency of a vibration of that class. We also observe, as is allowed by the selection rules (Part I, Section 6), the weak bands of series l and l′, in which the upper- and lower-state fundamental frequencies are found in combination, as 0—1 and 1—0 transitions, with the electronic and vibrational transitions of the main absorption origin A_0^0.

The following fundamental frequencies result from the evidence here presented:

$$E''(\text{H } 1)_{\text{ground}} = 710 \text{ cm.}^{-1} \qquad E''(\text{H } 1)_{\text{excited}} = 495 \text{ cm.}^{-1}$$

This vibration is moderately strong in the Raman effect; and in the Raman spectrum of liquid 1 : 3 : 5-trideuterobenzene it appears with the frequency 710·2 cm.$^{-1}$ (Herzfeld, Ingold, and Poole, *loc. cit.*).

(6) *Band Series* R, r, S, *and* s.—Series R contains a number of characteristic bands, of which the parent R_0^0, lies 1360 cm.$^{-1}$ above A_0^0. A single, much weaker band, S_0^0, is found the same distance above B_0^0. We assume the interval 1360 cm.$^{-1}$ to represent the first overtone of a vibration in the upper electronic state. From comparisons with the spectra of other benzenes (Part XI), we identify the vibration as the third member of the E'' symmetry class. Its fundamental frequency is

$$E''(\text{H } 2)_{\text{excited}} = 680 \text{ cm.}^{-1}$$

A number of bands of series A and B have weak companions displaced to lower frequencies by 30 cm.$^{-1}$. These constitute the series r and s, respectively. The interval must represent the reduction of frequency which arises from the exchange of a lower-state vibrational quantum for an upper-state quantum of the same symmetry class—possibly of the same vibration. An appropriate combination between the two vibrations, $E''(\text{H } 1)_{\text{ground}} = 710$ cm.$^{-1}$ and $E''(\text{H } 2)_{\text{excited}} = 680$ cm.$^{-1}$, could therefore explain these bands. The Boltzman factor for such a transition would not be prohibitively small. Since the motions of the point-sets are mixed together in rather a complicated way in the out-of-plane vibration classes of 1 : 3 : 5-trideuterobenzene (Bailey *et al.*, *J.*, 1940, 225), and therefore probably in different ways in the two electronic states, one can understand, on the basis of Herzberg and Teller's extension of the Franck–Condon principle, how the replacement of one such vibration by another of the same symmetry class can sometimes occur with considerable intensity. However, the alternative possibility cannot be excluded that the drop of 30 cm.$^{-1}$ may represent the difference between the lower- and upper-state frequencies of one of those vibrations whose upper-state frequencies are not certainly (or not accurately) known. Taking account of the effect of Boltzmann factors on intensity, the only vibrations which one could consider in this connexion would be the two planar deuterium-bending vibrations, $A_2'(\text{H } 1)$ and $E'(\text{H } 2)$, and of these the second becomes excluded if our suggestions of Section 3 be accepted.

(7) *Band Series* T, T′, U, v, *and* W.—The progression T, of rather less than moderate intensity, starts with a band, T_0^0, situated 821 cm.$^{-1}$ above the main active origin A_0^0. A very weak band is visible about the same distance above B_0^0, but it is not sufficiently well measured to be included in the record. The interval 821 cm.$^{-1}$ we take to be an overtone frequency belonging to the excited electronic state. For reasons based partly on the internal evidence of the spectrum, and partly on comparisons with the absorption spectra of other benzenes (Part XI), we identify the vibration concerned as one of the A_2'' class—the nearest analogue in this D_{3h} benzene, to the $A_{2u}(\text{H})$ vibration, which consistently gives overtone progressions in the absorption and fluorescence spectra of the D_{6h} compounds, benzene and hexadeuterobenzene. Band T_0^0 arises from an upward 0—2 transition of the vibration $A_2''(\text{H } 1)$, in combination with those electronic and vibrational transitions which produce the active origin A_0^0.

The fundamental frequency of this vibration in the electronic ground state being independently known, one may easily recognise the prior excitation of the corresponding ground-state overtone in the production of the weak, but sharp, band T′, situated 1062 cm.$^{-1}$ below the orgin A_0^0. An extremely weak band is visible about the same distance below B_0^0, although we do not include it amongst our record of measured bands. Band T′, then, arises from an upward 2—0 transition of the vibration $A_2''(\text{H } 1)$, in combination with those electronic and vibrational transitions which characterise the origin A_0^0.

The U series consists of a number of weak bands negatively displaced from the stronger B bands by 119 cm.$^{-1}$. The presence of bands correspondingly related to A bands cannot be

verified, since any such bands would be overlapped by B bands and by L bands. The U bands are attributed to 1—1 transitions of the vibration A_2''(H 1), in combination with the electronic and vibrational transitions of the associated B bands. The interval 119 cm.$^{-1}$ is thus interpreted as the difference between the fundamental frequencies of the vibration A_2''(H 1) in the lower and upper electronic states.

The frequencies involved in these three series are consistent with one another, and determine the following fundamental frequencies:

$$A_2''(\text{H 1})_{\text{ground}} = 531 \text{ cm.}^{-1} \qquad A_2''(\text{H 1})_{\text{excited}} = 411 \text{ cm.}^{-1}$$

The ground-state frequency agrees, to within the limits of experimental error, with the value, 533 cm.$^{-1}$, given by the infra-red spectrum of 1 : 3 : 5-trideuterobenzene vapour (Bailey *et al.*, *loc. cit.*).

A band, v_0^0, lying 200 cm.$^{-1}$ below B_0^0, is found in both the absorption and the fluorescence spectra of 1 : 3 : 5-trideuterobenzene (cf. Part VII, Section 5). In the latter spectrum it is the parent of a series of weak bands. The presence of bands similarly connected with A_0^0 cannot be verified because the positions in which they would appear are occupied by bands of the D series. As seems necessary, we interpret the v bands by means of the assumption that a 1—1 transition of some characteristic vibration is superposed on the electronic and vibrational transitions of B_0^0, the observed frequency displacement representing the difference between the fundamental frequencies of the vibration in the lower and upper electronic states. A displacement as large as 200 cm.$^{-1}$ is likely to be connected with an out-of-plane vibration; and the only out-of-plane vibration which is not excluded by our existing information about their frequencies is the second of the A_2'' hydrogen vibrations, A_2''(H 2). Accordingly, we assume a 1—1 transition of this vibration. A more positive reason for the assignment will be given later, inasmuch as we shall show that it produces agreement with the product rule when comparisons are made with other benzenes (Part XI).

In the fluorescence spectrum of 1 : 3 : 5-trideuterobenzene, we find the A_2''(H 2) vibration also involved through its first overtone, in the lower electronic state: this overtone, of frequency 1831 cm.$^{-1}$, becomes excited in producing the bands of series V (Part VII, Section 5). The absorption and fluorescence spectra together therefore determine the following fundamental frequencies:

$$A_2''(\text{H 2})_{\text{ground}} = 915 \text{ cm.}^{-1} \qquad A_2''(\text{H 2})_{\text{excited}} = 715 \text{ cm.}^{-1}$$

Previous studies of the infra-red spectrum of 1 : 3 : 5-trideuterobenzene have also yielded the value 915 cm.$^{-1}$ for the ground-state frequency (Bailey *et al.*, *loc. cit.*).

Series W of the fluorescence spectrum consists of a number of weak bands displaced upwards from the stronger bands of the A series by 720 cm.$^{-1}$. We regard this interval as an upper-state overtone frequency. From its low value, and from comparisons with similar series in the absorption spectra of other benzenes (Part XI), we identify the vibration concerned as the trigonal, out-of-plane, carbon-vibration, A_2''(C), the third vibration of the A_2'' symmetry class, and the nearest analogue for this D_{2h} benzene of the vibration B_{2g}(C), whose overtone we find in the absorption spectra of both the D_{6h} benzenes. Thus the parent band, W_0^0, is interpreted by the assumption of an upward 0—2 transition of this vibration, in association with the electronic and vibrational transitions of A_0^0. We infer from this the following fundamental frequency:

$$A_2''(\text{C})_{\text{excited}} = 360 \text{ cm.}^{-1}$$

(8) *Band Series* X′, Y, Y′, *and* y.—We deal in this section with a number of high-frequency bands believed to depend on the excitation of the deuterium- and protium-stretching vibrations of the symmetry classes E' and A_1'. In the first place, the selection rules allow bands due to transitions from the " vibrationless " level of the electronic ground state to the one-quantum levels, in the electronically excited state, of the deuterium- and protium-stretching vibrations of the E' class. Actually, the presence of a band due to a 0—1 transition of the deuterium-stretching vibration, E'(H 1), cannot be verified: the vibration frequency, which can be determined in another way (below), is such that this band, lying 2330 cm.$^{-1}$ above the electronic origin, would coincide with the broad and strong band, E_1^0. On the other hand, the band due to a similar excitation of the protium-stretching vibration, E'(H 1′), is easily recognised in the rather prominent band X_0', the parent of series X′. This band lies 3085 cm.$^{-1}$ above the forbidden electronic origin: formally, it is an " active origin ", similar to A_0^0 and E_0^0, and possibly F_0^0.

The other two parent bands of high frequency which we might expect to appear with considerable intensity are those which would result from the superposition of an upward 0—1 transition of either of the totally symmetrical hydrogen-stretching vibrations upon the electronic and vibrational transitions of A_0^0. In fact, these bands can readily be identified. The excitation in the upper electronic state of the totally symmetrical deuterium-stretching vibration, A_1'(H), is represented by a very sharp band, of rather less than moderate intensity, called Y_0^0, the parent of series Y. It lies 2300 cm.$^{-1}$ above A_0^0. An analogous excitation of the totally symmetrical protium-stretching vibration, A_1'(H'), is unmistakably shown by a very sharp band, of medium intensity, called Y_0', which is particularly prominent by reason of its occurrence in a spectral region in which almost all other bands are much broadened and overlapped. Band Y_0' lies 3135 cm.$^{-1}$ above A_0^0.

One other high-frequency band remains to be considered, *viz.*, the weak, but sharp, band, y_0^0, lying 30 cm.$^{-1}$ above Y_0^0, and therefore 2330 cm.$^{-1}$ above A_0^0. It might be thought a possible choice for the assigment we have actually applied to Y_0^0; but for this we naturally selected the stronger of the two bands (Part I, Section 6). Its considerably weaker companion, y_0^0, we now explain by the assumption of a 0—1 transition of the deuterium-stretching vibration of the E' class, E'(H 1), in combination with the electronic and vibrational transitions of A_0^0. The selection rules allow the transition to occur with low intensity (Part I, Section 6). We consider that we can observe band y_0^0 at all only because of its proximity to the stronger band Y_0^0, from which it can derive intensity by resonance (Part I, Section 5). The appearance in the absorption spectrum of benzene of similar high-frequency companion bands was interpreted on the same lines (Part II, Section 7, Series S and T).

In the fluorescence spectrum of 1 : 3 : 5-trideuterobenzene we find bands, called X and X', which are considered to involve transitions from the " vibrationless " excited state to the fundamental levels, in the lower electronic state, of the deuterium- and protium-stretching vibrations of the E' class, *viz.*, E'(H 1) and E'(H 1'). These fluorescence bands lie 2290 and 3080 cm.$^{-1}$, respectively, below the electronic origin (Part VII, Section 6). From them, and from the absorption bands above discussed, we can deduce the following E' fundamental frequencies:

$$E'(\text{H 1})_{\text{ground}} = 2290 \text{ cm.}^{-1} \qquad E'(\text{H 1})_{\text{excited}} = 2330 \text{ cm.}^{-1}$$
$$E'(\text{H 1'})_{\text{ground}} = 3080 \text{ ,,} \qquad E'(\text{H 1'})_{\text{excited}} = 3085 \text{ ,,}$$

We also obtain the following A_1' fundamental frequencies of the excited state, which are compared below with the corresponding frequencies of the ground state [in brackets] as determined in the Raman spectrum of liquid 1 : 3 : 5-trideuterobenzene (Herzfeld, Ingold, and Poole, *loc. cit.*):

$$[A_1'(\text{H})_{\text{ground}} = 2282 \text{ cm.}^{-1}] \qquad A_1'(\text{H})_{\text{excited}} = 2300 \text{ cm.}^{-1}$$
$$[A_1'(\text{H'})_{\text{ground}} = 3053 \text{ ,, }] \qquad A_1'(\text{H'})_{\text{excited}} = 3135 \text{ ,,}$$

On the whole, the upper-state frequencies of both symmetry classes are higher than the corresponding ground-state frequencies. Differences in the same direction were found for the hydrogen-stretching frequencies of benzene and hexadeuterobenzene (Part II, Section 7 and Part IV, Section 7).

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101. *Excited States of Benzene. Part VII. Description and Analysis of the First Ultraviolet Band System of the Fluorescence Spectrum of* 1 : 3 : 5-*Trideuterobenzene.*

By ARTHUR P. BEST, CHRISTOPHER K. INGOLD, and CHRISTOPHER L. WILSON.

The ultraviolet fluorescence spectrum of 1 : 3 : 5-trideuterobenzene is described, and measurements of the frequencies of many bands are recorded. A complete vibrational analysis of the spectrum is given. A number of fundamental frequencies of both electronic states are recognised, and are assigned to vibrations.

(1) *Measurements.*—The 1 : 3 : 5-trideuterobenzene was a sample prepared by the trideuteration of aniline and subsequent deamination (Best and Wilson, *J.*, 1946, 239; cf. Part VI, Section 1). Its fluorescence spectrum was excited in a 25-cm. column of the vapour by means of the mercury resonance line, 2537 A. We used the spiral lamp and cell described previously (Ingold and Wilson, *J.*, 1936, 941). As heretofore, dilute acetic acid was employed as filter in order to keep out light of damagingly short wave-length, and any photochemical losses were made good by circulating the vapour through the cell between two reservoirs containing the liquid or solid material. The temperatures of the reservoirs controlled both the flow-rate and the pressure in the cell. The spectrograph was the same Littrow-pattern instrument as that used for the absorption measurements (Part VI, Section 1) : it was again maintained at 20·0°, but was now focused for the region 3150—2530 A. It is necessary to provide a pressure sufficient to quench the resonance spectrum, *i.e.*, to furnish, in sufficient frequency, the collisions which are needed to take away that excess of vibrational and rotational energy, above the thermally normal amount, which the newly excited molecule contains; so that it is not in an abnormally violent state of vibration and rotation when it fluoresces. The resonance spectrum was effectively quenched when the pure vapour of 1 : 3 : 5-trideuterobenzene was employed at 25 mm. At this pressure most of the fluorescence spectrum could be recorded in exposures ranging from 10 to 40 minutes.

Special measures had to be taken in order to deal with the spectral region in which the fluorescence band-system overlaps the absorption system; for in that region most of the fluorescence light is reabsorbed under the conditions described, with the result that the record is very incomplete. This difficulty was overcome following the general procedure devised by Cuthbertson and Kistiakowsky (*J. Chem. Physics*, 1936, **4**, 9) : first, the pressure of the 1 : 3 : 5-trideuterobenzene was reduced, with the result that, although the intensity of fluorescence was correspondingly diminished, the proportion of fluorescence light which became absorbed was also reduced, and, by the use of a sufficiently low pressure, could be made unimportant; then, the diminished photographic intensity was compensated by a suitable increase of exposure; and finally, the high collision frequency needed to quench the resonance spectrum was provided by the addition, to a sufficiently high pressure, of spectrally inert gas. A pressure of 1 : 3 : 5-trideuterobenzene amounting to 0·2 mm. was found to be sufficiently low : the resultant exposures, 24—48 hours, were not prohibitively long. For the quenching we employed nitrogen, which is less efficient for this purpose than 1 : 3 : 5-trideuterobenzene itself, so that a pressure of several hundred mm. was necessary. That being so, we introduced the nitrogen at atmospheric pressure for convenience. It was passed over the solid 1 : 3 : 5-trideuterobenzene at a controlled temperature, then through the fluorescence cell, and then through a tube cooled in liquid air for the recovery of the 1 : 3 : 5-trideuterobenzene.

The iron arc was employed for the production of comparison spectra. The spectrograms were evaluated in part directly by means of the microscope, but mainly in the form of microphotometer records, as described already for the absorption spectrum (Part VI, Section 1).

The general structure of the spectrum is like that of the fluorescence spectrum of benzene or hexadeuterobenzene (Part I, Section 4 and Fig. 1, p. 409), except for certain differences. The chief of these is that, just as in the absorption spectrum of 1 : 3 : 5-trideuterobenzene the successive members of the positively-running, totally symmetrical progressions show an increasing multiplicity as the upper-state quantum numbers increase (Part VI, Sections 1 and 2), so, in the fluoresecnce spectrum of this substance, the successive members of the negatively-running, totally symmetrical progressions exhibit increasing multiplicity as the lower-state quantum numbers increase. One observes the usual growth of complexity along the sequence due to n—n transitions of the low-frequency vibration (cf. Part II, Section 1; and following Parts). On the other hand, resonance phenomena do not produce such striking effects as are found in the fluorescence spectrum of benzene (Part III, Sections 2 and 6), and in this respect the present spectrum more closely resembles that of hexadeuterobenzene.

Table I contains our measured frequencies, corrected to vacuum, and visually estimated intensities. Assignments are given in terms of a literal notation, the key to which is in Tables II and III. The letter-symbols by which the various series of bands are denoted have been made to correspond as far as possible to those used to designate the band-series of the absorption spectrum. Series A, B, C, D, H, I, J, j, L, l′, M, N, Q, and v, are identical in the two spectra, except that totally symmetrical progressions run mainly in the positive direction in absorption, but mainly in the negative direction in fluorescence.

TABLE I.

Fluorescence Spectrum of 1 : 3 : 5-*Trideuterobenzene. Frequencies, Intensities, and Assignments* (*cf. Tables II and III*).

Freq. (cm.$^{-1}$).	Inty.	Assgnt.	Freq. (cm.$^{-1}$).	Inty.	Assgnt.	Freq. (cm.$^{-1}$).	Inty.	Assgnt.
38697·4	ms	A_0^0	36781·1	ms	A_{-2}^0	35334	w	$B_{-1-1'}^2$
613·4	mw	C_0^0	735	w	$A_{-1-1'}^0$	316	ww	N_{-2}^1
582	ww	L_0^0	705·8	mw	C_{-2}^0	299	ww	D_{-2}^2
567	ww	$B_{1'}^0$	698·0	ww	B_0^6	245	ww	$D_{-1-1'}^2$
544·6	m	A_0^1	686·0	ww	$A_{-2'}^0$	233·2	w	B_{-2}^3
480·0	mw	B_1^0, M_0^0	638·2	ss	B_{-1}^0	223	ww	
468·0	mw	C_0^1	586·9	ms	$B_{-1'}^0$	184	ww	$B_{-1-1'}^3$
454	w		555·1	ms	D_{-1}^0	166	ww	N_{-2}^2
401·6	w	D_1^0	502	mw	D_{-1}^0	148	ww	D_{-2}^3
394	mw	A_0^2	487·8	s	B_{-1}^1	126	ww	$B_{-2'}^3$
330	w	B_1^1, M_0^1	438·0	ms	$B_{-1'}^1$	104	ww	X_0'
323	w	C_0^2	424	w	N_{-1}^0	079	ww	B_{-2}^4
254	ww	D_1^1	403·7	mw	D_{-1}^1	072	ww	
246	w	A_0^3	348	ww	$D_{-1'}^1$	036	ww	$B_{-1-1'}^4$
240	w		337·6	ms	B_{-1}^2	016	ww	N_{-2}^3
184	w	B_1^2, M_0^2	289	mw	$B_{-1'}^2$	011	ww	
176	ww		281	w	N_{-1}^1	34996	ww	D_{-2}^4
105	ww	j_0^0	268	w		940	ww	X_{-1}^0
036	mw	H_0^0	252	w	D_{-1}^2	933	ww	B_{-2}^5
033	mw	J_0^1	198	ww	$D_{-1'}^2$	866·3	w	A_{-4}^0
37986	ww	I'	187·8	m	B_{-1}^3	856	ww	
968	w	Q_0^0	177·0	w		817	ww	$A_{-3-1'}^0$
957	ww	j_0^1	142	w	$B_{-1'}^3$	805	ww	V_{-1}^0
937	w	I_0^0	129	ww	N_{-1}^2	792	ww	C_{-}^0
889	mw	H_0^1	118	ww		770	ww	$A_{-2-2'}^0$
879	mw	J_0^2	101	ww	D_{-1}^3	730·4	mw	B_{-3}^0
805	ww	j_0^2	096	ww		678·0	w	B_{-2-1}^0
800	ww		051	ww	$D_{-1'}^3$	652·0	ww	D_{-3}^0
785	ww	I_0^1	035	w	B_{-1}^4	628	ww	$B_{-1-2'}^0$
740·0	ms	A_{-1}^0	023	ww		597	ww	$D_{-2-1'}^0$
637	ww	I_0^2	35971	ww	N_{-1}^3	578·0	w	B_{-3}^1
590·3	ss	B_0^0	966	ww		528	ww	$B_{-2-1'}^1$
507·9	ms	D_0^0	957	ww	D_{-1}^4	517	ww	N_{-3}^0
443·5	s	B_0^1	947	ww		477	ww	$B_{-1-2'}^1$
389	w	v_0^0	894	w	X_0^0	426·0	w	B_{-3}^2
377·7	mw	N_0^0	887	ww	B_{-1}^0	378	ww	B_{-2-1}^2
356·4	m	D_0^1	877	ww		366	ww	N_{-3}^1
348	mw		822·6	m	A_{-3}^0	349	ww	D_{-3}^2
295·3	ms	B_0^2	812·4	w		329	ww	$B_{-1-2'}^2$
284·1	m		775·6	w	$A_{-2-1'}^0$	290	ww	$D_{-2-1'}^2$
236	ww	v_0^1	759	w	V_0^0	267·9	w	B_{-3}^3
222·8	mw	N_0^1	746·4	w	C_{-3}^0	260·7	ww	
205·3	mw	D_0^2	737	ww	B_{-1}^6	231	ww	$B_{-3-1'}^3$
146·0	m	B_0^3	730	ww	$A_{-1-2'}^0$	212	ww	$B_{-3-1'}^3$, N_{-3}^2
134	mw		684·0	s	B_{-2}^0	209	ww	
084	ww	v_0^2	632·3	m	$B_{-1-1'}^0$	201	ww	D_{-3}^3
075·4	mw	N_0^2	603·6	mw	D_{-2}^0	190	ww	
057·9	mw	D_0^3	581·5	w	$B_{-2'}^0$	164	ww	$B_{-1-2'}^3$
36996·6	mw	B_0^4	550·0	w	$D_{-1-1'}^0$	125	ww	B_{-3}^4
990	w		533·4	m	B_{-2}^1	070	ww	$B_{-2-1'}^4$
983	w		483·3	mw	$B_{-1-1'}^1$	042	ww	D_{-3}^4
926	mw	N_0^3	469·3	w	N_{-2}^0	33981	ww	B_{-3}^5
907	w	D_0^4	451	w	D_{-2}^1	913·6	w	A_{-5}^0
852	mw	B_0^5	433	w	$B_{-2'}^1$	861·0	ww	$A_{-4-1'}^0$
844	w		398	ww	$D_{-1-1'}$	839	ww	C_{-5}^0
835	w		383·3	mw	B_{-2}^3	832	ww	

TABLE I—*contd.*

Freq. (cm.$^{-1}$).	Inty.	Assgnt.	Freq. (cm.$^{-1}$).	Inty.	Assgnt.	Freq. (cm.$^{-1}$).	Inty.	Assgnt.
33780·0	w	B^0_{-4}	33542	ww	D^1_{-4}	32960·9	ww	A^0_{-6}
725·4	w	$B^0_{-3-1'}$	524·6	ww	$B^1_{-3-2'}$	907·9	ww	$A^0_{-5-1'}$
702	ww	D^0_{-4}	474·6	ww	B^2_{-4}	833·7	ww	B^0_{-5}
673	ww	$B^0_{-2-2'}$	423	ww	$B^2_{-3-1'}$	773	ww	$B^0_{-4-1'}$
627·0	w	B^1_{-4}	415	ww	N^1_{-4}	687	ww	B^1_{-5}
575·3	ww	$B^1_{-3-1'}$	326	ww	B^3_{-4}	623	ww	$B^1_{-4-1'}$
566·7	ww	N^0_{-4}	176	ww	B^4_{-4}			

Note : The intensity symbols, and the numerical parts of the assignment symbols, are explained in the first Note beneath Table I of Part III, and in the Note under Table I of Part VI. The letter-symbols here used are defined in the following Tables.

TABLE II.

Fluorescence Spectrum of 1 : 3 : 5-*Trideuterobenzene. Key to Assignments* (*cf. Table I*).

	Freq. (cm.$^{-1}$).	p', p''.	q', q''.	s.
A	$= 38184 + 513 - 956p'' - 1005q'' - 150s$	0—6	0—2	0—3
B	$= \,,, - 594\{+ 893p' + 988q' - 956p'' - 1005q''\} - 150s$	0, 1 0—5	0, 1 0—2	0—6
C	$= \,,, + 2 \times 513 - 594 - 956p'' - 150s$	0—5		0—2
D	$= \,,, + 513 - 2 \times 594\{+ 893p' - 956p'' - 1005q''\} - 150s$	0, 1 0—4	0, 1	0—4
H	$= \,,, - 594 + 2 \times 223 - 150s$			0, 1
I	$= \,,, + 513 - 2 \times 373 - 150s$			0—2
J	$= \,,, - 150s$			1, 2
j	$= \,,, + 513 - 594 - 150s$			0—2
L	$= \,,, - 594 + 2 \times 495$			
l′	$= \,,, + 513 - 710$			
M	$= \,,, + 513 - 215 - 150s$			0—2
N	$= \,,, - 594 - 215 - 956p'' - 150s$	0—3		0—3
O	$= \,,, - 215$			
V	$= \,,, - 594 - 2 \times 915 - 956p''$	0, 1		
v	$= \,,, - 594 - 200 - 150s$			0—2
X	$= \,,, - 2290$			
X′	$= \,,, - 3080$			

TABLE III.

Fluorescence Spectrum of 1 : 3 : 5-*Trideuterobenzene. Assignment to Vibrations of the Vibration Frequencies* (*cm.*$^{-1}$) *contained in Table II.*

Upper-state fundamental frequencies (+).	Lower-state fundamental frequencies (−).	Diffs. of upper- and lower-state fundamentals (−).	Vibration.
593	956	—	A_1'(C)
988	1005	—	A_1'(C′)
—	915	200	A_2''(H 2)
513	594	81	E'(C 1)
—	2290	—	E'(H 1)
—	3080	—	E'(H′ 1)
223	373	150	E''(C)
495	710	215	E''(H 1)

(2) *Band Series* A, B, C, *and* D.—As usual, these four series constitute the main frame of the spectrum (Part I, Section 4). The form of development of the branching negative progression is much more immediately obvious than is that of the positive progressions of the absorption spectrum (Part VI, Section 2). One reason for this is that the progression frequencies of the electronic ground state (956 and 1005 cm.$^{-1}$), which are of main importance for fluorescence, lie closer together than do the corresponding frequencies of the excited state (893 and 988 cm.$^{-1}$), which have the same importance for absorption; and thus, in the fluorescence spectrum, the multiplets arising in the progressions are less interleaved with other systems than are the multiplets of the absorption spectrum. A second reason is that the fluorescence spectrum contains nothing corresponding to the E series of the absorption spectrum; in general, the fluorescence spectrum exhibits no particularly marked resonance effects.

These series confirm the already given values (Part VI, Section 2) for the frequency of the forbidden electronic origin, and for the frequencies of the fundamental vibrations E'(C 1), A_1'(C) and A_1'(C′) in both upper and lower electronic states.

(3) *Band Series* H, I, J, *and* j.—These series correspond closely to the identically named series of the absorption spectrum; and they contribute along with the absorption series to the

determination of the lower- and upper-state fundamental frequencies, 373 and 223 cm.$^{-1}$, of the vibration E''(C), as already noted in Part VI, Section 4.

Series H consists of a negative sequence in 150 cm.$^{-1}$, running from a band H_0^0, lying 446 cm.$^{-1}$ above B_0^0. The transitions are from the second and higher quantum levels of the E'' (C) vibration of the upper electronic state, two such quanta being lost, whilst an E'(C 1) quantum of the lower electronic state is gained. The band I_0^0, situated 760 cm.$^{-1}$ below A_0^0, the parent of series I, is assumed to involve the loss of an E'(C 1) quantum in the upper state, and the acquisition of two E''(C) quanta in the lower state. Series J consists of a sequence in 150 cm.$^{-1}$ running negatively as if from the electronic origin, except that no band in this position appears. As usual, we assume 1—1, 2—2, . . . transitions of the vibration E''(C). Series j is another negative sequence in 150 cm.$^{-1}$, which runs from a band j_0^0 situated 79 cm.$^{-1}$ below the electronic origin. Here we assume 1—1, 2—2, . . . , transitions of the vibration E''(C), superposed on 1—1 transitions of the vibration E'(C 1).

(4) *Band Series* L, l′, M, N, *and* Q.—These series correspond closely to the identically named series of the absorption spectrum (Part VI, Section 5). They all involve an excitation of the vibration E''(H 1) in either or both electronic states; and they contribute, together with the absorption series, to the determination of the fundamental frequencies, 710 and 495 cm.$^{-1}$, of this vibration in the ground and excited electronic states.

The band L_0^0, which is found 992 cm.$^{-1}$ above B_0^0, is explained by the assumption of a downward 2—0 transition of this vibration, combined with a downward 0—1 transition of the vibration E'(C 1). The very weak band l′, situated 711 cm.$^{-1}$ below A_0^0, is assumed to involve a downward 0—1 transition of the vibration E''(H 1) in association with a downward 1—0 transition of the vibration E'(C 1). Series M and N consist of bands negatively displaced by 215 cm.$^{-1}$ from the stronger bands of series A and B respectively. They are explained by assuming 1—1 transitions of the vibration E''(H 1), in combination with the electronic and vibrational transitions which characterise the bands of series A and B. The band Q_0^0, which lies 216 cm.$^{-1}$ below the electronic origin, is considered to arise from a 1—1 transition of the vibration E''(H 1) between states in which no other vibration is excited.

(5) *Band Series* V *and* v.—The progression V starts with a band V_0^0 lying 1831 cm.$^{-1}$ below the main active origin B_0^0. We interpret the interval as the first overtone of the vibration A_2''(H 2), the fundamental frequency of which is known, from the infra-red spectrum, to be 915 cm.$^{-1}$ (Bailey *et al.*, *J.*, 1946, 255). Thus the band V_0^0 is assumed to be formed in a downward 0—2 transition of this vibration, in association with a 0—1 transition of the vibration E'(C 1).

The series labelled v consists of a number of weak bands lying 200 cm.$^{-1}$ below some of the strongest bands of series B. The parent band, v_0^0, of series v is also found in the absorption spectrum. For reasons explained in Part VI, Section 7, we regard the v bands as involving 1—1 transitions of the vibration A_2''(H 2), in combination with the transitions of the associated B bands. The interval, 200 cm.$^{-1}$, thus represents the difference between the fundamental frequencies of this vibration in the ground and the excited electronic states.

Thus, series V and v, taken together, provide the values already quoted in Part VI, Section 7, for the fundamental frequencies of the vibration A_2''(H 2) in the two electronic states, *viz.*, the frequencies 915 and 715 cm.$^{-1}$.

(6) *Band Series* X *and* X′.—The hydrogen-stretching vibrations appear to be excited only very weakly in this spectrum. We might expect the excitation, in the lower electronic state, of the totally symmetrical deuterium- and protium-stretching vibrations to be signalised by bands displaced by their known fundamental frequencies below the main active origin B_0^0. Actually, weak bands appear very close to these positions, but they can be interpreted as belonging to other series, and are therefore so assigned.

The excitation, in the lower electronic state, of the degenerate deuterium- and protium-stretching vibrations of the class E' is, however, represented by the distinct, though weak, bands of series X and X′. The bands X_0^0 and X_0' are found 2290 and 3080 cm.$^{-1}$, respectively, below the electronic origin. We assume that they arise in transitions from the " vibrationless " level of the electronically excited state to the fundamental levels of the vibrations E'(H 1) and E'(H 1′), respectively, in the lower electronic state. The intervals 2290 and 3080 cm.$^{-1}$ are thus interpreted as the fundamental frequencies of these two vibrations. The values given by Herzfeld, Ingold, and Poole (*J.*, 1946, 332), partly on the evidence of the Raman spectrum of the liquid, and partly on that of the infra-red spectrum of the vapour, were 2292 and 3084 cm.$^{-1}$ (cf. Part VI, Section 8).

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102. *Excited States of Benzene. Part VIII. Description and Analysis of the First Ultraviolet Band System of the Absorption Spectrum of* 1 : 4-*Dideuterobenzene.*

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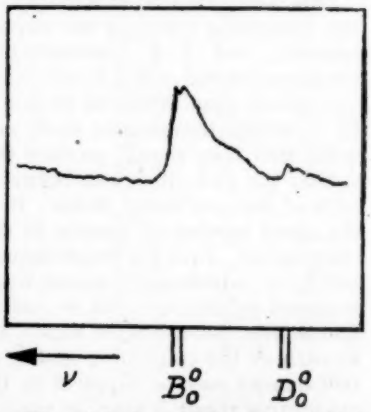
The ultraviolet absorption spectrum of 1 : 4-dideuterobenzene is described, and measurements of the frequencies of many bands are recorded. A complete vibrational analysis of the spectrum is given. The isotopic loading in this molecule produces a splitting into two distinct vibrations of each of those vibrations which are degenerate in the hexagonally symmetrical benzenes. Some spectral effects of the resolved degeneracies are pointed out. Eighteen fundamental frequencies of the upper electronic state and seven of the lower state are recognised, and all are assigned to their vibrations. Part of the theoretical basis of the assignments is given, the remainder being reserved for treatment in Part XI.

(1) *Measurements.*—The 1 : 4-dideuterobenzene was prepared from *p*-dibromobenzene in two stages by treatment of Grignard derivatives with deuterium oxide (Weldon and Wilson, *J.*, 1946, 235). The absorption spectrum of its vapour in the near-ultraviolet was recorded and evaluated exactly as described for 1 : 3 : 5-trideuterobenzene (Part VI, Section 1).

We shall first notice the general characteristics of the spectrum. Broadly, it is similar to that of benzene or hexadeuterobenzene, having the same four main series, involving positive progressions and negative sequences (cf. Part I, Section 4 and Fig. 1, p. 409). The notable effect, observed with 1 : 3 : 5-trideuterobenzene, of having two strongly progression-forming frequencies which together produce a rapidly developing complexity along the progressions, is not apparent in the absorption spectrum of 1 : 4-dideuterobenzene, because this has only one strong progression-forming frequency. However, this spectrum has its own particular complications, all of which arise from the splitting into two of certain vibrations which were doubly degenerate in benzene, hexadeuterobenzene, and 1 : 3 : 5-trideuterobenzene. The effect is to produce more complicated bands, as well as more bands, though this descriptive distinction is arbitrary from the point of view of analysis. The progressions are on the whole more complicated than are those of benzene and hexadeuterobenzene, but it is the sequences, rather than the progressions, along which one observes a very rapidly developing complexity.

Fig. 1.

Reproduction of part of a microphotometric record of the absorption spectrum of 1 : 4-*dideuterobenzene, showing the double-headed bands.*



The original record had to be rephotographed and intensified several times in order to obtain a line thick enough for the preparation of a block. The very fine line of the original record resolved the band heads much more clearly than does the reproduction. The region depicted runs from about 37430 *cm.*$^{-1}$ *to* 37670 *cm.*$^{-1}$.

We may describe the last-mentioned peculiarities more fully. Part of the effect arises from the circumstance that the main perturbing vibration, on which spectral activity depends, is degenerate in benzene, hexadeuterobenzene, and 1 : 3 : 5-trideuterobenzene, and becomes replaced in 1 : 4-dideuterobenzene by two similar, but distinct vibrations, whose frequencies fall apart by a few wave-numbers both in the electronic ground state and in the excited state. The result is that some of the simplest bands in the spectra of benzene, hexadeuterobenzene, and 1 : 3 : 5-trideuterobenzene become replaced by doubled bands, whilst more complicated bands have their complexity increased, in the spectrum of 1 : 4-dideuterobenzene. Thus the bands of the main progressions of series A and B in the absorption spectrum of benzene and hexadeuterobenzene are simply constituted: they involve the excitation, in one or other of the combining states, of only a single quantum of the degenerate perturbing vibration, and, otherwise, only one or more quanta of the totally symmetrical, progression-forming vibration: such bands, at our degree of resolution, appear more or less smoothly shaded to red from a single outstanding head on the short-wave side. In the absorption spectrum of 1 : 4-dideuterobenzene, each such band is replaced by two bands so strongly overlapped as to produce the appearance of a single band with two equal heads a few wave-numbers apart on the short-wave side. Fig. 1 illustrates the character described. It is merely for convenience, and particularly for the sake of reducing the total number of equations

necessary to represent the spectrum, that we give such double-headed bands a single label, even though we know that their two intensity maxima are produced by vibrationally distinct transitions.

A second perturbing vibration is that which produces band-series E in the absorption spectra of benzene, hexadeuterobenzene, and 1 : 3 : 5-trideuterobenzene. This vibration is also degenerate, and in 1 : 4-dideuterobenzene its place is taken by two vibrations, whose frequencies, in either electronic state, fall apart by about 20 cm.$^{-1}$. The result is that each of the E bands of benzene, hexadeuterobenzene, or 1 : 3 : 5-trideuterobenzene becomes replaced in the absorption spectrum of 1 : 4-dideuterobenzene by two neighbouring bands. To these more widely separated bands we have given distinctive names: the lower-frequency members of the band-pairs we collectively call series E, whilst the remaining members form our series E′.

A similar duplication may arise in the case of those series which, in benzene, hexadeuterobenzene, and 1 : 3 : 5-dideuterobenzene, involve, besides the primary activating vibration, an excitation, in either electronic state, of the first overtone of a degenerate vibration. Series G, for example, is characterised by the excitation, additionally to the main perturbing vibration, of a degenerate first overtone in the upper electronic state. In 1 : 4-dideuterobenzene the vibration, which is thus excited as its overtone, becomes split into two vibrations, whose overtones in the upper electronic state lie 44 cm.$^{-1}$ apart. Thus, corresponding to each G band, we find two bands separated by this interval. We call the lower-frequency members of the band-pairs series G, and the upper-frequency members series G′.

Some of the most striking effects of the loss of degeneracy appear in the sequences; for the chief sequence-forming vibration of benzene, hexadeuterobenzene, and 1 : 3 : 5-trideuterobenzene is degenerate, and in 1 : 4-dideuterobenzene becomes replaced by two sequence-forming vibrations, whose frequencies, in either electronic state, are fairly well separated. One result of this duplexity arises in those sequences which start from bands, such as those of the main progressions A and B, which owe their spectral activity to an independent perturbing vibration. In such cases the stronger bands, indeed all the observed bands, constitute what we call a " simply branching " sequence, that is, one formed under the restriction that the same sequence-forming vibrations are present with the same quantum numbers in the upper and the lower electronic states. There are two one-quantum bands, three two-quantum bands, and so on, in such a sequence, because one quantum of a sequence-forming vibration can be supplied in two ways, and two quanta of such vibrations in three ways, and so on; and because the two combining states are identically constituted with respect to such vibrations.

More complicated effects appear where the main cause of spectral activity is the presence in the combining states of the sequence-forming quanta themselves. In benzene, hexadeuterobenzene, and 1 : 3 : 5-trideuterobenzene the degenerate sequence-forming vibration itself produces a series called J, which appears when, in the absence of other non-totally symmetrical vibrations, equal numbers of quanta of this vibration are present in the two combining states. In 1 : 4-dideuterobenzene there are two sequence-forming vibrations, and all that matters, in order that they should produce the type of spectral activity which we associate with series J, is that the two vibrations between them should furnish the same total number of quanta to each of the combining states: it is unnecessary that each vibration separately should supply the same number of quanta to each state: whether they do or do not, the intensities are comparable. Thus the simple sequences of series J in the spectra of benzene, hexadeuterobenzene, and 1 : 3 : 5-trideuterobenzene become replaced in the spectrum of 1 : 4-dideuterobenzene by a sequence exhibiting what we call " complex branching ". There are now four one-quantum bands, nine two-quantum bands, and so on; because one quantum can be supplied in two ways to each of the combining states, and the alternatives are independent of each other; whilst two quanta can be supplied in three ways to each state, independently; and so on. The qualitative result is that, in place of the few, well-spaced, relatively strong bands of series J, as seen in the absorption spectrum of benzene, hexadeuterobenzene, or 1 : 3 : 5-trideuterobenzene, we find in the spectrum of 1 : 4-dideuterobenzene the total intensity distributed in a close array of many weaker bands.

Our detailed observations are recorded in Table I. Frequencies (corrected to vacuum) and intensities are expressed with the conventions used previously (cf. Part VI, Section 1). The vapour pressures corresponding to the temperatures mentioned in the column of intensities are computed to be approximately as follows: at 20°, 74 mm.; at − 10°, 15 mm.; at − 30°, 4 mm.

Assignments are expressed, as usual, by means of a literal notation. The letter-symbols are furnished with subscripts and superscripts, which represent the quantum numbers, in either electronic state, of the vibrations A_g(C), A_u(C), and B_{1u}(C), as explained in the Note beneath

Table I. The letters themselves distinguish those vibrational changes which are peculiar to the different band-series: they are defined by the equations of Table II, which also records the observed ranges of the above-mentioned quantum numbers. The vibration frequencies contained in the equations of Table II are assigned to vibrations in Table III. The meanings of the

TABLE I.

Absorption Spectrum of 1 : 4-*Dideuterobenzene. Frequencies, Intensities, and Assignments* (*cf. Tables II and III*).

Freq. (cm.$^{-1}$).	Inty. (20°).	Assgnt.	Freq. (cm.$^{-1}$).	Inty. (−10°).	Assgnt.	Freq. (cm.$^{-1}$).	Inty. (−30°).	Assgnt.
36582	ew	B_{-1}^{0-0}	37924	ew	j_0^{1-1}	38988·2	mw	$G_0'^{1'-1'}$
586	ew	F_0^{0-0}	953·6	w	$j_0^{1'-1}$	998	w	$G_0'^{1-1}$
	Inty. (−10°).		971	w	$J_0^{1-1'}$	39016·4	w	
			994·5	w	$J_0^{1'-1'}$	045·4	w	S_0^{0-0}
37109	w	$B_0^{21'-21'}$	38015	w	J_0^{1-1}	066·0	w	
129·3	vw	B_0^{2-2}	033·6	w	$J_0^{1'-1}$	084·5	mw	
166·8	w	$D_0^{11'-11'}$	052	vw	$H_0'^{0-0}$	098·8	mw	G_0^{0-0}
184	w	D_0^{2-2}	098·2	mw	$M_0^{11'-11'}$	108·8	mw	
240·1	mw	$B_0^{2'-2'}$	103	mw		138·0	mw	
252·7	mw	$B_0^{11'-11'}$		Inty. (−30°).		142·5	mw	$G_0'^{0-0}$
263	mw	B_0^{2-2}				148·2	mw	
270	mw		241·5	vw	$M_0^{1'-1'}$	154·2	mw	
292·7	w	N_0^{0-0}	279·2	vw	$C_0^{11'-11'}$	182·4	vw	U_0^{0-0}
309	w	$D_0^{1'-1'}$	353	w	$A_0^{2'-2'}$	187·1	vw	
318·2	w		367·6	ms	$A_0^{11'-11'}$	198·5	w	T_0^{0-0}
326·3	w	D_0^{1-1}	382·1	ms	A_0^{2-2}	207·7	vw	C_1^{2-2}
336	vw		405·4	w	M_0^{0-0}	218·5	vw	$B_2^{1'-1'}$
393·7	ms	$B_0^{1'-1}$	426·4	mw	$C_0^{1'-1'}$	229·1	vw	$B_2^{1-1'}$
399·6	ms		434	w		236·8	vw	
408·3	ms	B_0^{1-1}	449	vw	C_0^{1-1}	268·8	mw	$A_1^{11'-11'}$
413·5	ms		466·6	w	B_1^{0-0}	281·2	mw	A_1^{2-2}
419·2	vw	$B_0^{1'-1}$	511·1	s	$A_0^{1'-1'}$	288·8	mw	
425·0	w		519·5	ms	A_0^{1-1}	295·6	w	R_0^{2-2}
467·3	ms	D_0^{0-0}	526·3	ms		316·3	w	M_1^{0-0}
472·8	ms		580	ms	C_0^{0-0}	323·4	w	$C_1^{1'-1'}$
552·6	s	B_0^{0-0}	586·0	ms		339·5	w	C_1^{1-1}
558·1	s		665·0	vs	A_0^{0-0}	355·5	w	
597	w	C_{-1}^{0-0}	670·7	vs		377·9	w	B_2^{0-0}
612	w		701·5	vw	ω_0^{0-0}	385	vw	Q_0^{0-0}
685·7	ms	A_{-1}^{0-0}	722	ew	P_0^{0-0}	412·6	s	$A_1^{1'-1'}$
692·6	ms		728	ew		427·0	s	A_1^{1-1}
701	vw	$J_0^{21'-21'}$	754	ew	$G_0^{2'-2'}$	433·5	s	
710	ew	$j_0^{2-2'}$	764	ew		441·7	m	R_0^{1-1}
727	vw	J_0^{2-2}	776·1	vw		449·0	w	$E_0^{1'-1'}$
738	ew	$j_0^{2-11'}$	783	vw	$G_0^{11'-11'}$	466·6	w	
744	ew	$J_0^{21'-2}$	795	ew		485	ms	C_1^{0-0}
762	vw	$J_0^{12'-2}$	802	ew		494·3	ms	
770·6	vw	j_0^{2-2}	806	ew	G_0^{2-2}	501·4	m	$E_0'^{1-1}$
785	vw	$J_0^{2'-2}$	815	ew		525·8	mw	
795·3	vw	$J_0^{2-2'}$	828·0	vw	$G_0'^{2'-2'}$	536·0	w	K_0^{0-0}
808·8	vw	$J_0^{11'-2'}$	839	ew	$G_0'^{11'-11'}$	573·9	vs	A_1^{0-0}
825·6	vw	$J_0^{2-11'}$	848	ew		579·6	vs	
834·6	vw	$J_0^{2'-2'}$	866	ew	$G_0'^{2-2}$	587·5	m	R_0^{0-0}
845	ew	$J_0^{11'-11'}$	872	ew		605	vw	ω_1^{0-0}
865·5	w	J_0^{2-2}	914·9	w	$G_0^{1'-1'}$	623·5	mw	E_0^{0-0}
873·4	w	$J_0^{2'-11'}$	930·2	w		632·7	mw	
887·4	w	$J_0^{11'-2}$	939	w		642·6	m	$E_0'^{0-0}$
902·6	vw	$j_0^{1'-1'}$	947·0	w	G_0^{1-1}	662·3	m	
912·5	w	$J_0^{2'-2}$	958	w		696	vw	O_0^{1-1}

TABLE I—*contd.*

Freq. (cm.$^{-1}$).	Inty. (−30°).	Assgnt.	Freq. (cm.$^{-1}$).	Inty. (−30°).	Assgnt.	Freq. (cm.$^{-1}$).	Inty. (−30°).	Assgn.
39705·7	w	W_0^{0-0}	40480·1	vs	A_2^{0-0}	41458	w	$E_2'^{0-0}$
728·2	vw	z_0^{0-0}	490·8	vs		479·2	w	
829·4	mw	O_0^{0-0}	507·9	m	X_0^{0-0}	492·0	vw	O_2^{1-1}
836·8	mw		523	ew	ω_2^{0-0}	501	vw	
855·3	vw	$G_1^{1'-1'}$	530·8	mw	E_1^{0-0}	530	vw	W_2^{0-0}
862·1	vw	G_1^{1-1}	544·3	mw		545·4	vw	z_2^{0-0}
875·0	vw		549·8	m	$E_1'^{0-0}$	636	mw	O_2^{0-0}
899·1	vw	$G_1'^{1'-1'}$	570·0	m		641·8	mw	
904·7	vw		599	vw	O_1^{1-1}	653·6	mw	
967	vw	S_1^{0-0}	617·2	w	W_1^{0-0}	782·4	w	L_2^{0-0}
976·1	w	L_0^{0-0}	637·4	vw	z_1^{0-0}	796	mw	$Y_0''^{0-0}$
992·5	vw	G_1^{0-0}	641·4	vw		803·1	mw	
40017·5	w		731·1	mw	O_1^{0-0}	843	vw	G_3^{0-0}
050·1	w	$G_1'^{0-0}$	735·5	mw		853	vw	$G_3'^{0-0}$
053·0	w		743·7	mw		867	w	
065·3	w		754·6	vw	$G_2^{1'-1'}$	914	vw	T_3^{0-0}
075	ew	I_0^{0-0}	770	ew	G_2^{1-1}	985·3	w	$A_4^{11'-11'}$
082	ew		789·6	vw		997·4	w	
092	ew	U_1^{0-0}	868·6	vw	S_2^{0-0}	42009·6	vw	A_4^{2-2}
096	ew		881·1	w	L_1^{0-0}	132·7	mw	$X_1'^{0-0}$
107·0	w	T_1^{0-0}	890·5	w		141	mw	$A_4^{1'-1'}$
128·6	vw	$B_3^{1'-1}$	918·8	w	G_2^{0-0}	146	mw	
149	ew	B_3^{1-1}	930·4	w		154·8	w	A_4^{1-1}
185·3	mw	A_2^{2-2}	964	vw	$G_2'^{0-0}$	256	w	K_2^{0-0}
190·3	mw		970·4	vw		297·5	m	A_4^{0-0}
212·7	mw	V_0^{0-0}	977	vw		305	m	
224·8	vw	M_2^{0-0}	41010	w	T_2^{0-0}	548·5	w	O_3^{0-0}
257	vw	C_2^{1-1}	028	vw	Y_0^{0-0}	556·1	w	
260·2	vw		125	vw	V_1^{0-0}	700·3	w	$Y_1''^{0-0}$
285·6	w	B_3^{0-0}	229·4	mw	$X_0'^{0-0}$	713·5	w	
326·1	ms	$A_2^{1'-1'}$	240	mw	$A_3^{1'-1'}$	754·6	vw	G_4^{0-0}
331·3	s		258·7	mw	A_3^{1-1}	768	vw	$G_4'^{0-0}$
342·6	ms	A_2^{1-1}	271·8	w	$E_2^{1'-1'}$	784·6	vw	
346·6	s		283	w		43049·0	mw	$A_5^{1'-1'}$
358·3	m	$E_1^{1'-1'}$	354	w	K_2^{0-0}	060	w	A_5^{1-1}
374	w		386	s	A_3^{0-0}	068	w	
403·0	vw	C_2^{0-0}	393	s		171	w	K_4^{0-0}
407·0	vw		405	m	X_1^{0-0}	200	mw	A_5^{0-0}
415·3	vw	$E_1'^{1-1}$	428·5	vw	ω_3^{0-0}	211	mw	
418·4	vw		443·5	w	E_2^{0-0}			
441	vw	K_1^{0-0}	448·1	w				

Note: In the assignment column, the quantum numbers of the progression-forming, A_g(C), vibration are shown as subscripts, an implied positive sign referring to the upper electronic state, and a negative sign to the ground state. These upper- and lower-state quantum numbers are called p' and p'', respectively, in Table II. The quantum numbers of the two sequence-forming vibrations, B_{1u}(C) and A_u(C), are shown as superscripts, the former without dashes, and the latter with dashes, an implied positive sign again referring to the upper electronic state, and a negative sign to the lower state. These quantum numbers are expressed by a contracted notation in Table II. The common number of quanta of the vibration B_{1u}(C) in both states is called s, whilst the common number of quanta of the vibration A_u(C) in both states is called t; and a common number of quanta referring to the vibration A_u(C) in the upper state and B_{1u}(C) in the lower is termed u, whilst a common number of quanta with the reverse distribution of vibrations is termed v. In series J, s, t, u, and v cannot *all* be zero simultaneously, since J_0^{0-0} is forbiddden.

vibration symbols in this Table will be made clear by reference to Part I, Section 7, especially to Table V in that Section (p. 415). (For diagrams of the vibrations, see *J.*, 1946, pp. 278—299.)

The band-series A—E, G, H, J, M, and N correspond as closely as the different symmetries of the molecules allow to the identically named series of the absorption spectra of benzene,

hexadeuterobenzene, and 1 : 3 : 5-trideuterobenzene. Where, in the spectrum of 1 : 4-dideuterobenzene, two similar series arise from a resolved degeneracy, the one with the higher frequencies is distinguished by means of a dash : E, E′ and G, G′. Certain other series have been named to correspond as closely as possible to identically named series in the absorption spectrum of benzene. These are series F, O, P, and U : corresponding series are not observed in the spectrum of hexadeuterobenzene (cf. Parts II, IV, and VI).

TABLE II.

Absorption Spectrum of 1 : 4-*Dideuterobenzene. Key to Assignments* (*cf. Table I*).

	Freq. (cm.$^{-1}$.)	*p′*.	*p″*.	*s*.	*t*.	*u*.	*v*.
A	$= 38154 + \left\{\begin{matrix}511\\516{\cdot}5\end{matrix}\right\} + 909p' - 978p'' - 143s - 161t$	0—5	0, 1	0—2	0—2		
B	$= \,,, - \left\{\begin{matrix}596\\601{\cdot}5\end{matrix}\right\} + 909p' - 978p'' - 143s - 161t$	0—3	0, 1	0—3	0—2		
C	$= \,,, + \left\{\begin{matrix}511\\516{\cdot}5\end{matrix}\right\} + \left\{\begin{matrix}(511-596)\\(516{\cdot}5-601{\cdot}5)\end{matrix}\right\} + 909p' - 978p'' - 143s - 161t$	0—2	0, 1	0—2	0, 1		
D	$= \,,, + \left\{\begin{matrix}(511-596)\\(516{\cdot}56-01{\cdot}5)\end{matrix}\right\} - \left\{\begin{matrix}596\\601{\cdot}5\end{matrix}\right\} - 143s - 161t$			0—2	0, 1		
E	$= \,,, + 1469 + 909p' - 161t$	0—2			0, 1		
E′	$= \,,, + 1489 + 909p' - 143s$	0—2		0, 1			
F	$= \,,, - 1568$						
G	$= \,,, + \left\{\begin{matrix}511\\516{\cdot}5\end{matrix}\right\} + 2 \times 222 + 909p' - 143s - 161t$	0—4		0—2	0—2		
G′	$= \,,, + \left\{\begin{matrix}511\\516{\cdot}5\end{matrix}\right\} + 2 \times 243 + 909p' - 143s - 161t$	0—4		0—2	0—2		
H′	$= \,,, - \left\{\begin{matrix}596\\601{\cdot}5\end{matrix}\right\} + 2 \times 243$						
J	$= \,,, - 143s - 161t - 122u - 182v$			0—3	0—2	0—22	0—2
j	$= \,,, + \left\{\begin{matrix}511\\516{\cdot}5\end{matrix}\right\} - \left\{\begin{matrix}596\\601{\cdot}5\end{matrix}\right\} - 143s - 161t - 122u$			0—2	0, 1	0, 1	
K	$= \,,, + \left\{\begin{matrix}511\\516{\cdot}5\end{matrix}\right\} + 2 \times 435 + 909p'$	0—4					
L	$= \,,, + \left\{\begin{matrix}511\\516{\cdot}5\end{matrix}\right\} + 2 \times 655 + 909p'$	0—2					
l	$= \,,, + \left\{\begin{matrix}511\\516{\cdot}5\end{matrix}\right\} + 2 \times 706$						
M	$= \,,, + \left\{\begin{matrix}511\\516{\cdot}5\end{matrix}\right\} - 265 + 909p' - 143s - 161t$	0—2		0, 1	0, 1		
N	$= \,,, - \left\{\begin{matrix}596\\601{\cdot}5\end{matrix}\right\} - 265$						
O	$= \,,, + \left\{\begin{matrix}511\\516{\cdot}5\end{matrix}\right\} + 2 \times 585 + 909p' - 143s$	0—3		0, 1			
P	$= \,,, - \left\{\begin{matrix}596\\601{\cdot}5\end{matrix}\right\} + 2 \times 585$						
Q	$= \,,, + \left\{\begin{matrix}511\\516{\cdot}5\end{matrix}\right\} + 2 \times 357$						
R	$= \,,, + \left\{\begin{matrix}511\\516{\cdot}5\end{matrix}\right\} + 2 \times 457 - 143s$			0—2			
S	$= \,,, + 2 \times 457 + 909p'$	0—2					
T	$= \,,, + 457 + 585 + 909p'$	0—3					
U	$= \,,, + \left\{\begin{matrix}511\\516{\cdot}5\end{matrix}\right\} + \left\{\begin{matrix}511\\516{\cdot}5\end{matrix}\right\} + 909p'$	0, 1					
V	$= \,,, + \left\{\begin{matrix}511\\516{\cdot}5\end{matrix}\right\} + 2 \times 775 + 909p'$	0, 1					
W	$= \,,, + 2 \times 775 + 909p'$	0—2					
ω	$= \,,, + \left\{\begin{matrix}511\\516{\cdot}5\end{matrix}\right\} + 775 - 736 + 909p'$	0—3					
X	$= \,,, + 2355 + 909p'$	0, 1					
X′	$= \,,, + 3075 + 909p'$	0, 1					
Y	$= \,,, + \left\{\begin{matrix}511\\516{\cdot}5\end{matrix}\right\} + 2355$						
Y″	$= \,,, + \left\{\begin{matrix}511\\516{\cdot}5\end{matrix}\right\} + 3132 + 909p'$	0, 1					
z	$= \,,, + 2 \times 787 + 909p'$	0—2					

Note: The frequency 38154 cm.$^{-1}$ is that of the electronic origin. The other frequencies are vibration frequencies, which are assigned to vibrations in Table III, and in the Note thereunder. The frequencies in braces are to be read alternatively. The symbols for quantum numbers are defined in the Note beneath Table I.

TABLE III.

Absorption Spectra of 1 : 4-*Dideuterobenzene. Assignment to Vibrations of the Vibration Frequencies (cm.$^{-1}$) contained in Table II.*

Upper-state fundamental frequencies (+).	Lower-state fundamental frequencies (−).	Diffs. of upper- and lower-state fundamentals (−).	Vibration.
909	978	69	A_g(C)
511	596	85	A_g(C 1)
1489	—	—	A_g(C 2)
2355	—	—	A_g(H 1)
3132	—	—	A_g(H 2)
243	—	161	A_u(C)
706	—	—	A_u(H)
516·5	601·5	85	B_{1g}(C 1)
1469	1568	—	B_{1g}(C 2)
3075	—	—	B_{1g}(H 2)
222	—	143	B_{1u}(C)
435	—	—	B_{1u}(H 1)
655	—	—	B_{1u}(H 2)
585	—	265	B_{2g}(H)
357	—	—	B_{2g}(C)
457	—	—	B_{2g}(H 1)
775	—	—	B_{2g}(H 2)
787	—	—	B_{2u}(H 1)

Note: By the addition of one-quantum of the A_g(C 1) vibration to one, and one of the B_{1g}(C 1) vibrations to the other of the two combining states, differences of 80 cm.$^{-1}$ and 90 cm.$^{-1}$ may arise. Similarly, by the addition of one quantum of the A_u(C) vibration to one state, and one of the B_{1u}(C) vibration to the other, differences of 122 cm.$^{-1}$ and 182 cm.$^{-1}$ follow, which appear explicitly in equations J and j of Table II. Concerning the frequency 787 cm.$^{-1}$, see the text (Section 9).

(2) *Band Series* A—D.—As with the spectra described in the preceding papers, so also with the present spectrum, the four band series A—D provide the main structure (Part I, Section 4). Here, band series A and B involve 0—1 and 1—0 transitions, respectively, in either of the two distinct, but similar, planar, ring-bending vibrations, A_g(C 1) and B_{1g}(C 1); whilst series C and D depend on 1—2 and 2—1 transitions, respectively, of the same vibrations (Part I, Section 7). These transitions directly produce the four active origins A_0^{0-0}, B_0^{0-0}, C_0^{0-0}, D_0^{0-0}. From these origins progressions in the totally symmetrical vibration A_g(C) proceed, mainly in the positive direction, although some one-quantum members of corresponding negative progressions can be seen, much weakened by their Boltzmann factors. From the stronger bands of these progressions run " simply branching " sequences (cf. Section 1), always in the negative direction: they are due to n—n transitions in either of the distinct but similar, out-of-plane vibrations A_u(C) and B_{1u}(C).

We may first consider the effect of the duplexity of the origin-forming vibrations. All those bands of series A and B which are suitable for detailed observation can be seen as close doublets (cf. Fig. 1). The doublet separation in series A will represent the difference between the fundamental frequencies of the vibrations A_g(C 1) and B_{1g}(C 1) in the upper electronic state; and the separation in series B will represent the corresponding separation in the electronic ground state (cf. Fig. 2).

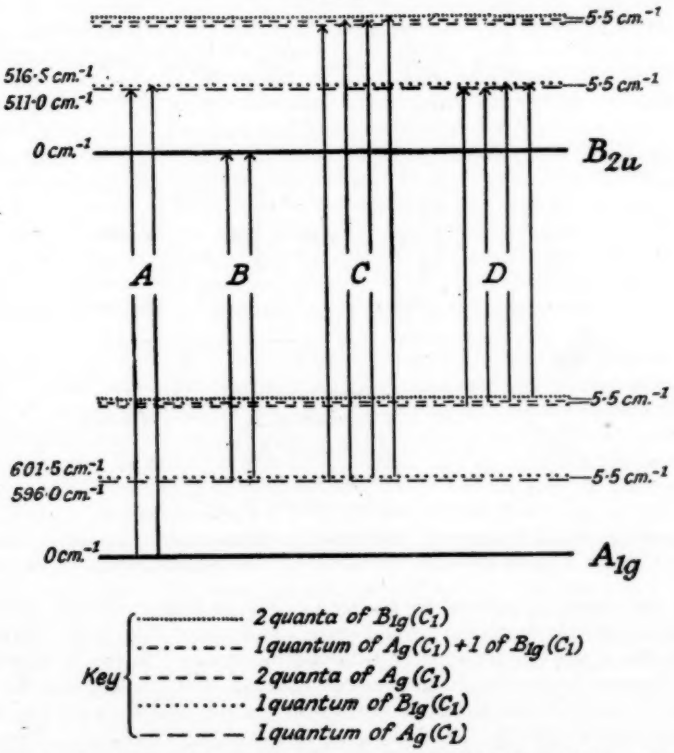
The bands of series C and D also appear as doublets, although they could in principle (cf. Part I, Section 7) be sextets, since two vibrational levels in one state are available to combine each with each of three vibrational levels of the other state (cf. Fig. 2). There are two reasons for the observed simplification. One is that those transitions which are strong enough for our observation always proceed by the simple loss or gain of an A_g(C 1) or B_{1g}(C 1) quantum, and not by the substitution of a pre-excited quantum of either kind by one of the other kind. This restriction reduces the six possible transitions to four (cf. Fig. 2). The further reason is that the separation between the A_g(C 1) and B_{1g}(C 1) frequencies in the upper electronic state happens to be identical with their separation in the lower state to within the errors of observation, with the result that the four transition frequencies coincide in pairs. This will be clear from Fig. 2.

Our value for the frequency separation of the A_g(C 1) and B_{1g}(C 1) vibrations, alike in the upper state and in the ground state, is 5·5 cm.$^{-1}$; and so sharp are the heads of the best doublet bands that this figure is likely to be reliable to within a few tenths of a wave-number. Now Herzfeld, Hobden, Ingold, and Poole attempted to estimate this frequency separation for the electronic ground state by resolution of the corresponding doublet Raman line (*J.*, 1946, 276).

Their value was 4·3 cm.$^{-1}$ (cf. Poole, *J.*, 1946, 245, and especially Fig. 1 of his paper); but they remarked (*loc. cit.*, p. 276, footnote) that this estimate was likely to be low, because the overlap of the components of the doublet was large in relation to the spectral width of each component. The present work confirms that the error was in the anticipated direction, and gives an indication of its magnitude.

Discussing vibrations in the electronic ground state, Herzfeld, Hobden, Ingold, and Poole (*loc. cit.*) gave three reasons for assigning the lower of the Raman doublet frequencies to the A_g(C 1) vibration, and the upper one to the B_{1g}(C 1) vibration. One of these reasons, that which was based on the forms of the normal co-ordinates, applies equally well to the electronically excited state. In any case it would seem that the dynamical factors which separate the frequencies, when the benzene molecule is loaded as it is in 1 : 4-dideuterobenzene, are likely to work the same way in both states. Accordingly, we assume that the lower of the fundamental

FIG. 2.



Scheme of energy levels and transitions, illustrating the doublet structure of the main bands of Series A—D in the absorption spectrum of 1 : 4*-dideuterobenzene.* (*Not to scale.*)

doublet frequencies of the upper electronic state belongs to the A_g(C 1) vibration, whilst the upper doublet frequency belongs to the B_{1g}(C 1) vibration.

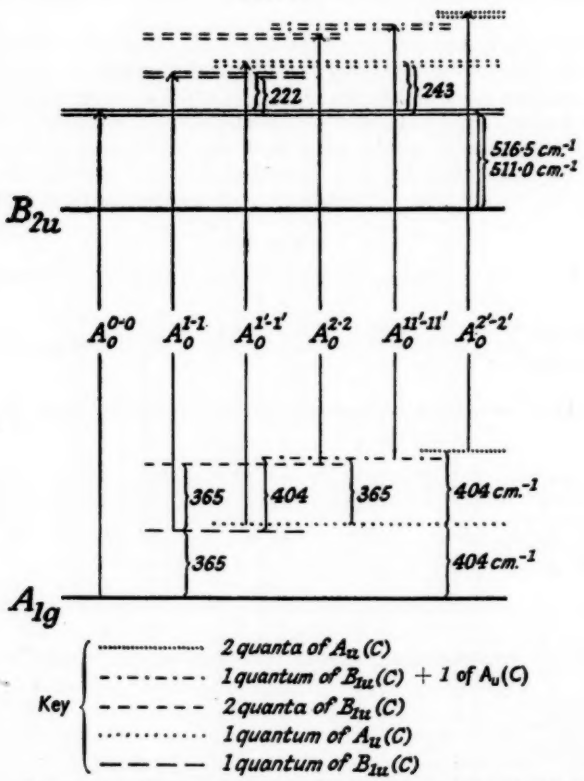
The progressions in the totally symmetrical frequencies, A_g(C), require no special comment: except for the fact that they maintain the doublet character described, they are as simple as for benzene or hexadeuterobenzene. For positive progressions the repeating interval is 909 cm.$^{-1}$; for negative progressions the interval is 978 cm.$^{-1}$.

The negative sequences of series A—D involve two sequence intervals, each of which may either repeat itself, or add itself to the other, to form a " simply branching " sequence, the bands of which are doublets for the reasons already given. The structure of such sequences is illustrated, for the case of a sequence of series A, in Fig. 3.

The two sequence intervals are 161 cm.$^{-1}$ and 143 cm.$^{-1}$. Each represents the difference between the fundamental frequencies of a vibration in the lower and the upper electronic states. Each belongs to one of the vibrations, A_u(C) and B_{1u}(C), into which the main sequence-forming vibration of benzene, hexadeuterobenzene, or 1 : 3 : 5-trideuterobenzene splits when its degeneracy

is broken down by the particular form of isotopic loading which is present in 1 : 4-dideuterobenzene (Part I, Section 7). Now it is not an accident that the upper sequence interval, 161 cm.$^{-1}$,

FIG. 3.



Scheme of energy levels and transitions, illustrating the development of a simply branching doublet sequence in Series A of the absorption spectrum of 1 : 4-*dideuterobenzene.* (*Not to scale.*)

is identical with the sequence interval for benzene. For, as Bailey, Carson, Gordon, and Ingold explained in relation to the electronic ground state, one form of the $E_u^{\pm}$(C) vibration of benzene is identical with the A_u(C) vibration of 1 : 4-dideuterobenzene : in these vibrations, the atoms which differ in the two molecules do not move (*J.*, 1946, 298, cf. diagram XIV, p. 299). Of course, the same is true for the electronically excited state, and thus we can at once identify the difference frequency, 161 cm.$^{-1}$, as belonging to the A_u(C) vibration. The other difference frequency, 144 cm.$^{-1}$, must belong to the B_{1u}(C) vibration. One should expect this to be lower, because, whilst in the A_u(C) vibration all the hydrogen motion is in the light hydrogen atoms, in the B_{1u}(C) vibration much of it is in the heavy hydrogen atoms; this will reduce, in similar proportion, the fundamental frequencies of the latter vibration in both electronic states, and therefore, also the corresponding frequency difference.

The above-discussed series determine the position of the forbidden electronic origin,

$$J_0^{0-0} = 38154 \pm 1 \text{ cm.}^{-1}$$

and the following fundamental vibration frequencies,

A_g(C 1)$_{\text{ground}}$ = 596 cm.$^{-1}$	A_g(C 1)$_{\text{excited}}$ = 511 cm.$^{-1}$
B_{1g}(C 1)$_{\text{ground}}$ = 601·5 cm.$^{-1}$	B_{1g}(C 1)$_{\text{excited}}$ = 516·5 cm.$^{-1}$
A_g(C)$_{\text{ground}}$ = 978 cm.$^{-1}$	A_g(C)$_{\text{excited}}$ = 909 cm.$^{-1}$

The ground-state frequencies as found in the Raman spectrum of liquid 1 : 4-dideuterobenzene are as follows : A_g(C 1) = 596·6 cm.$^{-1}$, B_{1g}(C 1) = 600·9 cm.$^{-1}$, A_g(C) = 978·0 cm.$^{-1}$ (Herzfeld, Ingold, and Poole, *J.*, 1946, 272).

(3) *Band Series* E, E′, *and* F.—The band series E and E′ are similar to the E bands of the absorption spectra of the three benzenes already studied (Parts II, IV, and VI). They lie just above the bands of the main progression, starting with the second member. As usual, they are double bands, the component of lower frequency being the stronger. In the present spectrum, however, we find twice the accustomed number of such bands, and they occur in pairs, overlapping slightly. They do not exhibit the narrow doublet splitting (5·5 cm.$^{-1}$) shown by the bands of series A—D, indeed, by most of the series in this spectrum.

We assume these band-pairs to be formed in 0—1 transitions of the two distinct, but closely similar vibrations, B_{1g}(C 2) and A_g(C 2), into which the degenerate carbon stretching vibration of benzene, hexadeuterobenzene, or 1 : 3 : 5-trideuterobenzene splits up when deuterium atoms are arranged as in 1 : 4-dideuterobenzene (Part I, Section 7). We assume also that, just as with the E bands of other absorption spectra, all the present E and E′ bands gain most of their intensity by resonance with the neighbouring A bands; and that they probably suffer an upward frequency-displacement as a result of the resonance (cf. Part II, Section 3). For this reason, we take, as heretofore, the lower and stronger intensity maximum of each band as giving the better approximation to the unperturbed position of its vibrational origin.

The lower frequency members of the pairs of bands form series E, the parent band of which, E_0^{0-0}, lies 1469 cm.$^{-1}$ above the electronic origin. The remaining members form series E′, the parent of which, $E_0'^{0-0}$, is found 1489 cm.$^{-1}$ above the origin. We tentatively assign the former series to the B_{1g}(C 2) vibration and the latter to the A_g(C) vibration. The reason for this choice is the same as that which Herzfeld, Hobden, Ingold, and Poole gave in relation to the electronic ground state (*loc. cit.*), *viz.*, that we should expect the B_{1g}(C 2) vibration to have the lower frequency since much of the motion is in the CD-groups, whereas in the A_g(C 2) vibration the motion is largely concentrated in the CH-groups. We take it that the same applies to the upper electronic state, in which the vibrations have the frequencies given by the frequency intervals quoted. However, this argument neglects the possibility of disturbance by assumed resonance displacements, and is therefore uncertain in its application to the electronically excited state.

Since the assignment, first proposed by Sponer and her collaborators, of the E bands of benzene to 0—1 transitions of the vibration E_g^+(C 2), was later considered doubtful by her (cf. Part II, Section 3), it seems worth noting that the duplication of this series, which we observe in the absorption spectrum of 1 : 4-dideuterobenzene (and, as we shall see later, in the spectrum of monodeuterobenzene), is strong evidence in favour of the original assignment; especially as the separation of the frequencies, into which the upper-state E_g^+(C 2) frequency must be assumed to split in 1 : 4-dideuterobenzene and monodeuterobenzene, is just of the sort of magnitude which we should expect on the basis of the known splitting which these frequencies suffer in the electronic ground state.

The extremely weak band F_0^{0-0}, found at the long-wave end of the spectrum, 1568 cm.$^{-1}$ below the electronic origin, is assigned to a 1—0 transition of the vibration B_{1g}(C 2). Its weakness must be associated with its very small Boltzmann factor. A band $F_0'^{0-0}$, due to a 1—1 transition of the vibration A_g(C 2), which is expected to appear about 1587 cm.$^{-1}$ below the origin, is probably present, but it was not measured, because it could not with certainty be distinguished from the tail of another very weak, long-wave band, B_1^{0-0}.

These bands provide the following fundamental frequencies:

$$A_g(\text{C 2})_{\text{ground}} = (1587\ \text{cm.}^{-1}) \qquad A_g(\text{C 2})_{\text{excited}} = 1489\ \text{cm.}^{-1}$$
$$B_{1g}(\text{C 2})_{\text{ground}} = 1568\ \text{cm.}^{-1} \qquad B_{1g}(\text{C 2})_{\text{excited}} = 1469\ \text{cm.}^{-1}$$

The frequency in parenthesis, not satisfactorily observed in the absorption spectrum, is derived from the Raman spectrum of liquid 1 : 4-dideuterobenzene. The other ground-state frequency, as given by the Raman spectrum, is 1569 cm.$^{-1}$ (Herzfeld, Hobden, Ingold, and Poole, *loc. cit.*), in good agreement with the value now recorded. The higher of the pair of excited-state frequencies lies above the corresponding frequency for benzene (1470 cm.$^{-1}$), but this irregularity may be due to the postulated resonance displacements, as suggested in Part II, Section 3.

(4) *Band Series* G, G′, H′, J, *and* j.—The bands of series G and G′ resemble the G bands of the absorption spectra of benzene, hexadeuterobenzene, and 1 : 3 : 5-trideuterobenzene (Parts II, IV, and VI). They have a similar, characteristically complex, shape: and they probably reproduce the doublet structure of A bands, superposed on their own special contours. They appear, as usual, between 400 cm.$^{-1}$ and 500 cm.$^{-1}$ above the stronger A bands; but now we find twice the accustomed number of them, and they occur as adjacent pairs. The lower-frequency members of the pairs form series G, and the others, series G′.

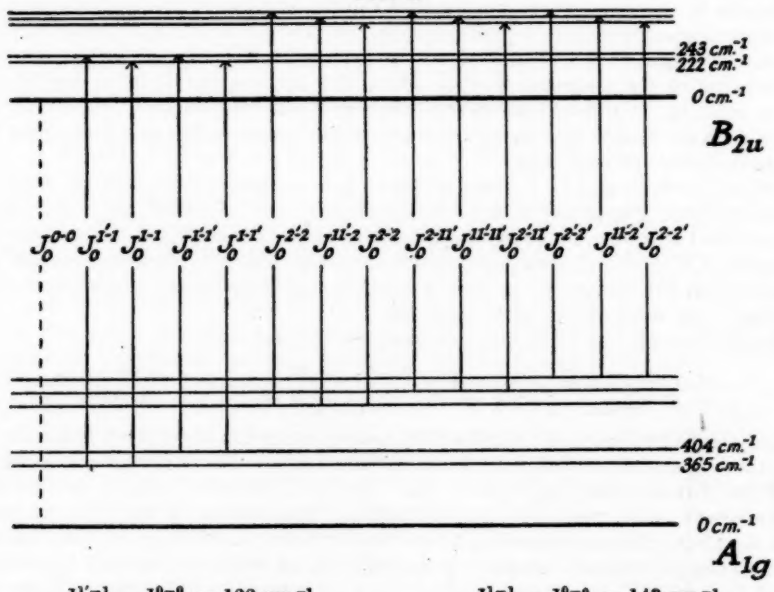
The G bands of benzene, hexadeuterobenzene, and 1 : 3 : 5-trideuterobenzene are explained by the assumption of an upward 0—2 transition of the degenerate, low-frequency vibration, superposed on those electronic and vibrational transitions which characterise the bands of series A. Analogously, we explain the bands of the present series G and G′ by assuming, in similar combination, upward 0—2 transitions of each of the vibrations, B_{1u}(C) and A_u(C), into which the degenerate low-frequency vibration splits, when deuterium atoms are disposed in the molecule as in 1 : 4-dideuterobenzene (cf. Part I, Section 7).

The bands of series G are situated approximately 445 cm.$^{-1}$ above, and those of series G′ about 485 cm.$^{-1}$ above, the related bands of series A. The two intervals represent overtone frequencies in the upper electronic state, one of the vibration B_{1u}(C) and the other of the vibration A_u(C). The larger interval is identical with the separation between G and A bands in the absorption spectrum of benzene. Accordingly we connect series G′ with the overtone of the vibration A_u(C), which, as we have already noted (Section 2), is identical with one form of the degenerate vibration, E_u(C), of benzene. The other series, G, is connected with the overtone of the vibration B_{1u}(C), which should have the lower fundamental frequency (Section 2), and therefore the lower overtone frequency.

The single band $H_0'^{0-0}$ probably marks the beginning of a double series, H, H′, related to B bands, as the double series G, G′ is to A bands. But no more of this assumed series can be seen, probably because, just below $H_0'^{0-0}$, the J series commences, the numerous bands of which nearly fill the spectrum for the next 300 cm.$^{-1}$ downward.

In the absorption spectra of benzene, hexadeuterobenzene, and 1 : 3 : 5-trideuterobenzene, the J series consists of a simple *n*—*n* sequence in the low-frequency, degenerate vibration. It runs negatively as if from the electronic origin except that the 0—0 band is absent, and may possibly be repeated after an interval corresponding to the upper-state frequency of the totally symmetrical vibration. In the corresponding series, J, of 1 : 4-dideuterobenzene, we have two vibrations, A_u(C) and B_{1u}(C), together taking the place of the degenerate vibration (Part I, Section 7). All possible pairs of their quanta are of comparable importance for the production of spectral activity, and therefore the J sequence is not dominated by the totally symmetrical combinations, as in general are sequences that start from a spectrally active origin. Accordingly, series J

FIG. 4.



$J_0^{1'-1} - J_0^{0-0} = 122$ cm.$^{-1}$. $J_0^{1-1} - J_0^{0-0} = 143$ cm.$^{-1}$.
$J_0^{1'-1'} - J_0^{0-0} = 161$ cm.$^{-1}$. $J_0^{1-1'} - J_0^{0-0} = 182$ cm.$^{-1}$.

Scheme of energy levels and transitions, illustrating the development of the complex branching sequence J of the absorption spectrum of 1 : 4-*dideuterobenzene.* (*Not to scale.*)

is not a simply branching sequence : it is a " complex branching " sequence, the mode of development of which can be followed with the aid of Fig. 4. The two vibrations in the two electronic

states produce four sequence intervals, as shown below the diagram, and these can be repeated or superposed on one another in every possible way. In Table I we mark all the four one-quantum bands, all the nine two-quantum bands, and five of the sixteen possible three-quantum bands, the series disappearing only as it runs beneath a rather strong band of series A. It may be noted that, unlike the majority of the bands in this spectrum, the bands of series J appear single-headed—as they well might, since they do not involve excitations of the doublet-forming vibrations, A_g(C 1) and B_{1g}(C 1).

A second complex branching sequence is present, but cannot be traced so fully. This is series j, to which we assign a constitution similar to that of series J except for the presence, additionally, of one quantum of one of the vibrations A_g(C 1) and B_{1g}(C 1) in each of the combining states. Thus series j is related to series J, just as C is to A, or as D is to B. Theoretically, series j starts from an active origin, but the 0—0 band, which would have only A_g(C 1) and B_{1g}(C 1) quanta, and not A_u(C) or B_{1u}(C) quanta, in its combining states, cannot be seen; so it is evident that the spectral activity of the series comes essentially, not from the single A_g(C 1) and B_{1g}(C 1) quanta, but from the repeating A_u(C) and B_{1u}(C) quanta, as it does in series J. We can therefore understand why totally symmetrical combinations of these quanta do not dominate the series, and why, accordingly, it shows " complex branching ", just as does the J series.

The upper-state overtone frequencies given by series G and G′, and the various difference frequencies of series J, and of sequences within other series (cf. Section 2), provide us with the following fundamental vibration frequencies:

$$A_u(\mathrm{C})_{\mathrm{ground}} = 404 \text{ cm.}^{-1} \qquad A_u(\mathrm{C})_{\mathrm{excited}} = 243 \text{ cm.}^{-1}$$
$$B_{1u}(\mathrm{C})_{\mathrm{ground}} = 365 \text{ cm.}^{-1} \qquad B_{1u}(\mathrm{C})_{\mathrm{excited}} = 222 \text{ cm.}^{-1}$$

The two A_u(C) frequencies agree with the E_u^+(C) frequencies for benzene, as determined in Part II. The two ground-state frequencies agree satisfactorily with previous estimates: Herzfeld, Ingold, and Poole's indirect estimate of the A_u(C) frequency was 405 cm.$^{-1}$ (*J.*, 1946, 319); whilst Bailey, Carson, Gordon, and Ingold's study of the infra-red fundamental band, B_{1u}(C), gave the frequency 367 cm.$^{-1}$, this value being necessarily rather rough, because part of the band was outside the long-wave limit of their apparatus (*J.*, 1946, 288).

(5) *Band Series* K, L, *and* l.—We deal with these three series next, because, according to our interpretations, they are connected with the remaining vibrations of the out-of-plane classes B_{1u} and A_u.

The bands of the main progression A, starting with the second member, are persistently accompanied on the low-frequency side by satellite bands, which collectively we call series K. Evidently the bands of series K are deriving their considerable intensity by resonance with the neighbouring A bands. This shows that their transitions, like those of the A bands, must start from the " vibrationless " ground state. We can explain such bands by assuming either the excitation of an upper-state frequency 870 cm.$^{-1}$, in combination with transitions of series A, or the excitation of an upper-state frequency 1385 cm.$^{-1}$ in combination with the electronic transition only. Taking account of the selection rules (Part I, Section 7), and making comparisons with other absorption spectra, especially with that of benzene itself (Part XI), we choose the former alternative, assigning the frequency 870 cm.$^{-1}$ as the first overtone of the vibration B_{1u}(H 1). Its nearest analogue in benzene is the hexagonal, out-of-plane, hydrogen vibration A_{2u}(H), which produces a very similar overtone series, also called K, in the absorption spectrum. It is natural to look for the 1—1 sequence bands of any vibration of rather low frequency, but such sequence bands of the B_{1u}(H 1) vibration would have the difference-frequency 162 cm.$^{-1}$, and would coincide with the prominent 1—1 bands of the vibration A_u(C) just as with benzene the A_{2u}(H) sequence bands cannot be observed since they coincide with those of the analogous vibration, E_u^+(C).

The progression of weak but moderately sharp bands, which constitute series L, starts with a band situated 1820 cm.$^{-1}$ above the electronic origin, or 1310 cm.$^{-1}$ above the main active origin A_0^{0-0}. One possible explanation would treat the separation from the electronic origin as the upper-state overtone frequency of the vibration A_g(C). Although the strict selection rules would allow this interpretation, we reject it on the ground that the fundamental frequencies of the A_g(C) vibration, taken in relation to the frequencies of the A_{1g}(C) vibration of benzene and hexadeuterobenzene, show that the former vibration must have very nearly perfect hexagonal symmetry, both in the ground and in the excited electronic states of 1 : 4-dideuterobenzene; so that it should not be excited to any appreciable extent in the absence of a suitable deforming vibration. Therefore we take the displacement from $A_0^{0-?}$ as the characteristic upper-state

frequency of series L, supposing this frequency to be excited in combination with the transitions of series A. Comparisons with other spectra, especially with the absorption spectrum of benzene (Part XI), lead us to assign this frequency as the upper-state first overtone of the vibration B_{1u}(H 2). Its nearest analogue in benzene is the vibration E^+_u(H), the upper-state overtone of which also records itself in the absorption spectrum. Any 1—1 sequence bands of the 1 : 4-dideuterobenzene vibration B_{1u}(H 2) could only be very weak, and would occur in positions in which they cannot be verified because of overlapping by stronger bands.

The following fundamental frequencies result from these assignments:

$$B_{1u}(\text{H 1})_{\text{excited}} = 435 \text{ cm.}^{-1} \qquad B_{1u}(\text{H 2})_{\text{excited}} = 655 \text{ cm.}^{-1}$$

As will be shown in Part XI, these values agree with the product rule. The corresponding ground-state frequencies are known from observations in the infra-red (Bailey, Carson, Gordon, and Ingold, *loc. cit.*); and they are as follows: B_{1u}(H 1) = 597 cm.$^{-1}$; B_{1u}(H 2) = 876 cm.$^{-1}$.

The single weak band 1^{0-0}_0, lying 1411 cm.$^{-1}$ above A^{0-0}_0, is assumed to arise by excitation, in the upper electronic state, of the first overtone of the vibration A_u(H), in combination with those electronic and vibrational transitions which characterise A^{0-0}_0. This assignment is based on the position of the band. A band in the same position, relatively to the active origin A^0_0, was found in the absorption spectrum of benzene, and was considered to involve, in combination with the transitions of A^0_0, an excitation in the upper state of the first overtone of the vibration E^+_u(H) (Part II, Section 8). Now, as Bailey, Carson, Gordon, and Ingold explained, with reference to the electronic ground state, one of the normal co-ordinates of the vibration E^+_u(H) of benzene is identical with the normal co-ordinate of the vibration A_u(H) of the 1 : 4-dideuterobenzene, and therefore the frequencies of the two vibrations are exactly equal (*J.*, 1946, 298; diagram XV, p. 299). The same is equally true for the electronically excited state; and therefore the assignment of the 1 : 4-dideuterobenzene band follows from that of the benzene band. Thus we arrive at another fundamental frequency of the upper state:

$$A_u(\text{H})_{\text{excited}} = 706 \text{ cm.}^{-1}$$

The corresponding ground-state frequency is, of course, the same as that of the ground-state E^+_u(H) frequency of benzene, *viz.*, 970 cm.$^{-1}$, as estimated by Herzfeld, Ingold, and Poole from Raman and infra-red combination tones (*loc. cit.*).

(6) *Band Series* M, N, O, *and* P.—Series M consists of a number of prominent bands negatively displaced from A bands by the uniform interval 265 cm.$^{-1}$. Series N consists of a single band similarly displaced from the parent band of series B. We assume these M and N bands to arise from 1—1 transitions of the out-of-plane hydrogen vibration B_{2g}(H), in combination with the electronic and vibrational transitions of the related A and B bands.

Series, also called M and N, which are very closely similar to these, and have identically the same displacement, 265 cm.$^{-1}$, from series A and B, were found in the absorption, and the fluorescence, spectra of benzene. The identity of the frequency displacement in the absorption and fluorescence spectra proved the presence of 1—1 transitions; and, years before we had seen the absorption spectra of any partly deuterated benzene, we had assigned these transitions to the out-of-plane, hydrogen vibration E^-_g(H)—mainly on the basis of the isotope shift of series M and N in hexadeuterobenzene. It was satisfactory, therefore, that these series should appear again in the absorption spectrum of 1 : 4-dideuterobenzene, and yet again, as we shall see in Part X, in that of monodeuterobenzene, in both cases in exactly the same relative positions as those in which they occur in the spectra of benzene. Only three of the thirty vibrational degrees of freedom of a benzene molecule are completely identical in benzene, monodeuterobenzene, and 1 : 4-dideuterobenzene: the vibration we had chosen is one of them. The chosen vibration, called E^-_g(H) in benzene, A_2(H′) in monodeuterobenzene, and B_{2g}(H) in 1 : 4-dideuterobenzene, involves counter-rotatory motions of the carbon and hydrogen hexagons about a para-axis, so selected that it will contain any deuterium atoms (cf. *J.*, 1946, 285, diagram XII).

Series O consists of a number of prominent bands positively displaced from A bands by the interval 1170 cm.$^{-1}$. Series P consists of a single band similarly displaced from the parent band of series B. We suppose these O and P bands to arise from upward 0—2 transitions of the vibration B_{2g}(H), in combination with the electronic and vibrational transitions of the correlated A and B bands.

Closely similar series, also called O and P, with just the same displacement from series A and B, were found in the absorption spectrum of benzene. They were assigned to upward 0—2 transitions of the vibration E^-_g(H), in combination with the electronic and vibrational transitions

of series A and B, respectively. It is consistent that we find the same two series in the absorption spectrum of 1 : 4-dideuterobenzene, and again, as we shall see in Part X, in that of monodeuterobenzene : the common displacement, 1170 cm.$^{-1}$, is evidently the upper-state overtone frequency of a vibration which is identical in all three benzenes. This justifies our assignment. It is of interest that the O bands of 1 : 4-dideuterobenzene are on the whole distinctly narrower than are the O bands of benzene, even though the former have cause to be 5·5 cm.$^{-1}$ wider since they must include the doublet separation of series A. The difference bears out our interpretation (Part II, Section 6) of the considerable breadth of the benzene bands, which we assumed to be due, at least in part, to the splitting by anharmonicity of the higher-order degeneracy involved in the overtone of a degenerate vibration. The vibration of 1 : 4-dideuterobenzene is, of course, not degenerate.

These assignments* lead to the following fundamental frequencies :

$$B_{2g}(\mathrm{H})_{\mathrm{ground}} = 850 \text{ cm.}^{-1} \qquad B_{2g}(\mathrm{H})_{\mathrm{excited}} = 585 \text{ cm.}^{-1}$$

The ground-state frequency, as found in the Raman spectrum of liquid 1 : 4-dideuterobenzene is 849·5 cm.$^{-1}$ (Herzfeld, Hobden, Ingold, and Poole, *loc. cit.*).

(7) *Band Series* Q, R, S, T, V, W, *and* ω.—We group these series together because, according to our interpretations, they are all connected, in one way or another, with one of the three vibrations of the out-of-plane symmetry class B_{2g}.

The single weak band, Q_0^{0-0}, lies 714 cm.$^{-1}$ above the main active origin A_0^{0-0}. We assign the interval as the upper-state first overtone of the carbon vibration B_{2g}(C). The assignment is based on comparisons with other benzenes (cf. Part XI).

Series R commences with a band R_0^{0-0} situated 914 cm.$^{-1}$ above A_0^{0-0}. Progression S starts with a band S_0^{0-0} lying 914 cm.$^{-1}$ above the electronic origin. Comparisons with the spectra of other benzenes (Part XI) suggest that the common interval is the upper-state first overtone of the hydrogen vibration, B_{2g}(H 1). We recognise its fundamental frequency, 457 cm.$^{-1}$, again in the upper-state combination frequency 457 + 585 = 1042 cm.$^{-1}$, by which the initial band progression T is displaced above the electronic origin. These assignments are in accordance with the selection rules (Part I, Section 7). Series S and T are assumed to involve the excitation, without an activating vibration of the A_g or B_{1g} class, either of two quanta of the vibration B_{2g}(H 1), or of one quantum of this vibration and one of the vibration B_{2g}(H). Both these vibrations derive from the degenerate benzene vibration E_g^-(H), the excitation, without other vibrations, of the first overtone of which cannot be observed in the absorption spectrum of benzene because of overlapping, but is observed in the spectrum of hexadeuterobenzene, as also is the overtone of the analogous vibration, E''(H 1), in the spectrum of 1 : 3 : 5-trideuterobenzene.

Progression V begins with a band situated 1550 cm.$^{-1}$ above the active origin A_0^{0-0}. We ascribe it to a transition, like that of A_0^{0-0}, but with a superposed excitation of the upper-state frequency 1550 cm.$^{-1}$. Progression W starts with a band lying 1550 cm.$^{-1}$ above the electronic origin J_0^{0-0}. These bands are very sharp, a fact which is consistent with our assumption that the frequency of the characteristic upper-state vibration is to be measured by the displacement from the electronic origin, J_0^{0-0}, rather than from the doublet band A_0^{0-0}. For reasons based essentially on comparisons with other spectra (Part XI), we regard the common interval, 1550 cm.$^{-1}$, as the first overtone, in the upper electronic state, of the remaining B_{2g} vibration, *viz.*, B_{2g}(H 2). Tentatively, we suggest that one quantum of this upper-state vibration, and one of the lower-state vibration B_{2g}(H 1), are together involved in the production of the small positive interval which separates the very weak bands of series ω from the strongest bands of series A.

The above assignments lead to the following fundamental frequencies :

$$B_{2g}(\mathrm{C})_{\mathrm{excited}} = 357 \text{ cm.}^{-1} \qquad B_{2g}(\mathrm{H\ 1})_{\mathrm{excited}} = 457 \text{ cm.}^{-1}$$
$$B_{2g}(\mathrm{H\ 2})_{\mathrm{excited}} = 775 \text{ cm.}^{-1}$$

The values are in accordance with the product theorem. The corresponding ground-state frequencies have been measured in the Raman spectrum of liquid 1 : 4-dideuterobenzene; and

* We consider the main part of the intensity of series M and N to be due to 1—1 transitions of the vibration B_{2g}(H), rather than of the vibration A_u(H), which has the same difference frequency, first, because the Boltzmann factor of the former vibration is larger, and secondly, because in all these spectra one notices a general correlation of transition probabilities between overtone series and sequences, and the overtone series, O and P, of the vibration B_{2g}(H) are so much stronger than is the overtone series, l, of the vibration A_u(H). It is not excluded that a minor part of the intensity of series M and N comes from 1—1 transitions of the vibration A_u(H).

they are as follows: B_{2g}(C) = 634·1 cm.$^{-1}$; B_{2g}(H 1) = 736 cm.$^{-1}$; B_{2g}(H 2) = 967 cm.$^{-1}$ (Herzfeld, Hobden, Ingold, and Poole, *loc. cit.*).

(8) *Band Series* X, X′, Y, *and* Y″.—These are the series involving the deuterium- and protium-stretching vibrations of the electronically excited state. The selection rules (Part I, Section 7) allow three such fundamental vibrations to appear, *viz.*, a deuterium and a protium vibration of the A_g class, and a second protium vibration belonging to the B_{1g} class. It follows also from the selection rules that either these vibrations may be excited alone, or their excitation may be superposed on that of either of the more usual perturbing vibrations.

The excitation of the deuterium vibration, A_g(H 1), alone can be seen in series X, which starts with a band situated 2355 cm.$^{-1}$ above the electronic origin. The bands of this progression are very sharp, as suits our assumption that they do not involve the perturbing vibrations of series A or B, and therefore do not contain a corresponding doublet separation. The upper-state frequency to which we are led agrees well with the upper-state deuterium-stretching frequencies of hexadeuterobenzene and 1 : 3 : 5-trideuterobenzene as determined in Parts IV and VI.

The excitation of one of the protium vibrations alone—we identify it as the vibration B_{1g}(H 2)—is seen in the parent band series X′, which lies 3075 cm.$^{-1}$ above the electronic origin, and starts a two-membered progression. The bands of this progression are also very sharp, doubtless for the reason mentioned above. The existence of a band arising from the excitation alone of the other protium-stretching vibration, A_g(H 2), cannot be verified, since it would coincide with a band of series E.

The deuterium-stretching vibration, A_g(H 1), appears again in the assignment of a band Y_0^{0-0} situated 2355 cm.$^{-1}$ above the active origin A_0^{0-0}. We explain this band by assuming the excitation, in the upper electronic state, of the fundamental vibration, A_g(H 1), in combination with the electronic and vibrational transitions of A_0^{0-0}.

The B_{1g}(H 2) frequency 3075 cm.$^{-1}$ cannot be found in the form of a band displaced by this amount above A_0^{0-0}; for such a band would be overlaid by the prominent band O_2^{0-0}. On the other hand, the second protium-stretching vibration, A_g(H 2), is recognised in the assignment of the remaining high-frequency series, Y″. The parent band, $Y_0''^{0-0}$, is situated 3132 cm.$^{-1}$ above A_0^{0-0}, and starts a two-membered progression, the bands of which, though moderately sharp, appear to have a doublet structure similar to that of A_0^{0-0}. This is consistent with the view that the band $Y_0''^{0-0}$ involves an excitation, in the upper electronic state, of the vibration A_g(H 2), in combination with the electronic and vibrational transitions of the A_0^{0-0} doublet. The two upper-state protium-stretching frequencies, to which these assignments lead, are obviously in general agreement with the protium-stretching frequencies of benzene and 1 : 3 : 5-trideuterobenzene as determined in Parts II and VI.

It remains to be explained why we assign the upper of the two protium-stretching frequencies to the A_g vibration, and the lower to the B_{1g} vibration. There are two reasons. The first is the empirical analogy with the electronic ground state, in which the two corresponding frequencies stand in this order: these frequencies can be individually identified simply and with certainty by their polarisation in the Raman effect. The other reason is based on the theoretical consideration that the normal co-ordinate of the B_{1g} protium-stretching vibration (cf. *J.*, 1946, 284, diagram IX) is identical with one normal co-ordinate of the E_g^+ protium-stretching vibration of benzene—not exactly and of mathematical principle, as with some normal co-ordinates which have been discussed above, but to a degree of approximation which is made very close by the high frequency and weak coupling of protium-stretching vibrations. In confirmation we find that, in the electronic ground state, the B_{1g} protium-stretching frequency of 1 : 4-dideuterobenzene lies within five wave-numbers of the E_g^+ protium-stretching frequency of benzene. Now in the absorption spectrum of benzene we find both the A_{1g} and the E_g^+ protium-stretching frequencies of the electronically excited state; but there is a clear distinction between them, inasmuch as the latter only can be excited without an accompanying perturbing vibration. In this way we know that the E_g^+ protium-stretching frequency of the excited state of benzene is 3080 cm.$^{-1}$. Our frequency, 3075 cm.$^{-1}$, of the excited state of 1 : 4-dideuterobenzene is 5 cm.$^{-1}$ below this, just as the B_{1g} frequency of the ground state of 1 : 4-dideuterobenzene, 3042 cm.$^{-1}$, is 5 cm.$^{-1}$ below the E_g^+ frequency of the ground state of benzene, 3047 cm.$^{-1}$.

We may recapitulate these fundamental frequencies of the upper electronic state of 1 : 4-dideuterobenzene:

$$A_g(\text{H 1})_{\text{excited}} = 2355 \text{ cm.}^{-1} \qquad A_g(\text{H 2})_{\text{excited}} = 3132 \text{ cm.}^{-1}$$
$$B_{1g}(\text{H 2})_{\text{excited}} = 3075 \text{ cm.}^{-1}$$

The corresponding ground-state frequencies, as determined in the Raman spectrum of liquid 1 : 4-dideuterobenzene, are as follows: A_g(H 1) = 2280·0 cm.$^{-1}$; A_g(H 2) = 3055·0 cm.$^{-1}$; B_{1g}(H 2) = 3042 cm.$^{-1}$ (Herzfeld, Hobden, Ingold, and Poole, *loc. cit.*). It will be noted that all the upper-state frequencies are higher than the corresponding ground-state frequencies, as we have already found for the hydrogen-stretching vibrations of benzene, hexadeuterobenzene, and 1 : 3 : 5-trideuterobenzene (Parts II, IV, and VI).

(9) *Band Series* U *and* z.—Two band series remain, of which the first, U, has a counterpart in the absorption spectrum of benzene. It involves excitation in the upper electronic state of *two* quanta of the main perturbing vibration, A_g(C 1) and B_{1g}(C 1). Such even-quantum excitations should produce only weak spectral activity, and in fact the intensities of the bands of series U are very low.

The last series z can only tentatively be assigned. It is a three-membered progression of very weak bands, the first of which lies 1574 cm.$^{-1}$ above the electronic origin. It is not certain that these bands do not belong to series G, but they seem not to have the usual appearance of G bands nor the right intensity variation. If they are distinct, they cannot be explained solely in terms of independently determined frequencies, and thus must involve some additional upper-state frequency. Provisionally we may suggest the existence of an upper-state frequency, 787 cm.$^{-1}$, belonging to the planar deuterium-bending vibration, B_{2u}(H 1), the ground-state frequency of which is 814 cm.$^{-1}$ (Bailey, Carson, Gordon, and Ingold, *loc. cit.*). An excitation in the upper state of the first overtone of this vibration might be held responsible for the production of series z.

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103. *Excited States of Benzene. Part IX. Description and Analysis of the First Ultraviolet Band System of the Absorption Spectrum of* 1 : 2 : 4 : 5-*Tetradeuterobenzene.*

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The ultraviolet absorption spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene is described, and measurements of the frequencies of many bands are recorded. A complete vibrational analysis of the spectrum is offered. The spectral effects of resolved degeneracies are generally similar to those observed with 1 : 4-dideuterobenzene. Seventeen fundamental frequencies of the upper electronic state and seven of the lower state are recognised, and all are assigned to their vibrations. The basis of the assignment is partly given, completion being reserved for Part XI.

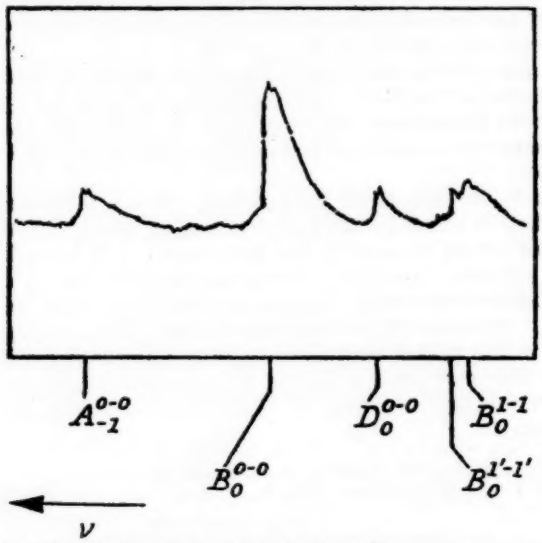
1) *Measurements.*—The 1 : 2 : 4 : 5-tetradeuterobenzene was prepared by deuteration of 1 : 4-dibromobenzene with heavy sulphuric acid, followed by debromination by means of the Grignard reaction, as described by Best and Wilson (*J.*, 1946, 239). The absorption spectrum of its vapour was photographed and measured, exactly as described for 1 : 3 : 5-trideuterobenzene.

In general, the spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene is similar to the absorption spectra of other benzenes: it has four main series, involving positive progressions and negative sequences, obviously having the usual type of interpretation (cf. Part I, Section 4, and Fig. 1, p. 409). The spectrum especially resembles that of 1 : 4-dideuterobenzene, *e.g.*, in its double-headed bands, illustrated in Fig. 1, in the display of certain series in duplicate, in the moderate growth of complexity along the progressions, and in the rapid development of complexity in the sequences. Our interpretation of these features is just the same as for 1 : 4-dideuterobenzene (cf. Part VIII, Section 1). The resemblances mentioned are only general: there are differences of detail, which will be discussed in the following sections. Moreover, in some of its weaker series, the spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene much more closely resembles the spectrum of hexadeuterobenzene than that of 1 : 4-dideuterobenzene; and this is especially true for some series whose analogues in the spectrum of 1 : 4-dideuterobenzene are very closely similar to series found in the absorption spectrum of benzene.

Our detailed observations are recorded in Table I, using the conventions previously employed (cf. Part VI, Section 1). The vapour pressures corresponding to the temperatures mentioned in the column of intensities are estimated to be approximately as follows: at 20°, 74 mm.; at 0°, 27 mm.; at −35°, 3 mm. In the column of assignments, quantum numbers are indicated according to the system used for the spectrum of 1 : 4-dideuterobenzene (cf. Part VIII, Section 1),

whilst the letter-symbols of the present spectrum are defined by the equations of Table II. The vibration frequencies in Table II are assigned to vibrations in Table III. The method of naming

FIG. 1.



Reproduction of part of a microphotometer record of the absorption spectrum of 1 : 2 : 4 : 5-*tetradeuterobenzene, showing the double-headed bands.*

The original record has been re-photographed and intensified several times in order to obtain a line thick enough for the preparation of a block. The original record resolves the band-heads much more clearly than does the reproduction. The region shown runs from about 37450 *cm.*$^{-1}$ *to* 37800 *cm.*$^{-1}$.

TABLE I.

Absorption Spectrum of 1 : 2 : 4 : 5-*Tetradeuterobenzene. Frequencies, Intensities, and Assignments* (*cf. Tables II and III*).

Freq. (cm.$^{-1}$).	Inty. (20°).	Assgnt.	Freq. (cm.$^{-1}$).	Inty. (0°).	Assgnt.	Freq. (cm.$^{-1}$).	Inty. (0°).	Assgnt.
36666	ew	B_{-1}^{0-0}	37671·9	w	C_{-1}^{0-0}	38203·9	w	$C_0^{12'-12'}$
676	ew		688·8	w		211	w	
	Inty. (0°).		761·8	m	A_{-1}^{0-0}		Inty. (−35°).	
			768·5	m				
37184	ew	$B_0^{12'-12'}$	797	ew	$J_0^{3'-3'}$	235	w	$B_1^{11'-11'}$
198	ew		808	ew	$J_0^{21'-12'}$	241·6	w	
209·9	ew	$B_0^{3'-3'}$	846	ew	$j_0^{11'-11'}$	266·0	w	$A_0^{21'-21'}$
256·4	vw	$D_0^{11'-11'}$	880	w	$J_0^{3'-2}$	272·3	w	
280·5	vw	N_0^{1-1}, $N_0^{1'-1'}$	906	w	$J_0^{2'-11'}$	282·3	mw	$A_0^{12'-12'}$
335	mw	B_0^{2-2}	922	w	J_0^{2-2}	294·1	mw	
343·3	mw	$B_0^{2'-2'}$	939	vw	$J_0^{2'-2'}$	344·1	vw	$C_0^{11'-11'}$
351·1	mw		948	vw	$J_0^{2-11'}$	352·8	vw	
399·3	mw	D_0^{1-1}	962	vw	$j_0^{1'-1}$	360	vw	$C_0^{2'-2'}$
406·7	mw	$D_0^{1'-1'}$	982	vw	j_0^{1-1}	365	vw	
425·7	mw	N_0^{0-0}	999	vw	$j_0^{1'-1'}$	381·8	mw	$B_1^{1'-1'}$
467·8	ms	B_0^{1-1}	38045·5	vw	$J_0^{1'-1}$	388	w	
481·2	ms	$B_0^{1'-1'}$	073·3	w	J_0^{1-1}	432·7	m	$A_0^{11-11'}$
493·7	ms		081·5	vw	$J_0^{1'-1'}$	437·6	mw	
499	vw	$k_0'^{0-0}$	086·9	vw	H_0^{0-0}	442·5	mw	$A_0^{2'-2'}$
506	vw		094·2	vw		450·4	mw	
546	m	D_0^{0-0}	103	vw	$J_0^{1-1'}$	457·4	vw	$K_0'^{0-0}$
550·6	m		117·6	w	$A_0^{23'-23'}$	468·5	vw	
627·8	s	B_0^{0-0}	124·7	vw				
632·8	s		140·0	mw	$A_0^{13'-13'}$			

TABLE I—*contd.*

Freq. (cm.$^{-1}$).	Inty. (−35°).	Assgnt.	Freq. (cm.$^{-1}$).	Inty. (−35°).	Assgnt.	Freq. (cm.$^{-1}$).	Inty. (−35°).	Assgnt.
38495·5	m	C_0^{1-1}	39535·5	m	C_1^{0-0}	40573·7	mw	X_0^{0-0}
500·3	m		542·5	m		630	ew	V_1^{0-0}
508·8	m	$C_0^{1'-1'}$	549·3	vw	$L_0'^{0-0}$	641	ew	
515	m	M_0^{0-0}	560·8	w	K_0^{0-0}	685·3	mw	R_1^{0-0}
524·6	m	B_1^{0-0}	566	w		700·9	mw	
528	m		604·2	w	A_1^{0-0}	795	mw	S_1^{0-0}
552	m	A_0^{1-1}	617·6	vs		808	mw	
566	ms		623·3	vs		999	mw	G_2^{0-0}
581·2	s	$A_0^{1'-1'}$	633·4	s	E_0^{0-0}	41009	m	U_2^{0-0}
589·6	ms		645·7	s		017·5	m	
599·6	w	k_0^{0-0}	714	vw	T_1^{0-0}	178·7	vw	C_3^{1-1}
642·9	ms	C_0^{0-0}	740·6	w	V_0^{0-0}	190	vw	
647·9	ms		747·4	w		203	vw	$C_3^{1'-1'}$
724·2	vs	A_0^{0-0}	768·2	ew	$G_1'^{2'-2'}$	207	vw	
728·5	vs		798·5	mw	R_0^{0-0}	260	m	$A_3^{1'-1'}$
759·9	w	κ	812	ew	$G_1^{2'-2'}$	280·7	m	
813	vw	T_0^{0-0}	830	vw		297	m	$E_2^{1'-1'}$
860·4	vw	$G_0'^{2'-2'}$	895·4	mw	$G_1'^{1'-1'}$	304	m	
872·7	vw		903·9	mw		343·6	w	C_3^{0-0}
974·5	w	$G_0'^{1-1}$	914·1	mw	S_0^{0-0}	394	ms	A_3^{0-0}
990·1	w		937·0	vw	G_1^{1-1}	415	s	
39002·4	mw	$G_0'^{1'-1'}$	951·8	vw	$G_1^{1'-1'}$	427·0	m	E_2^{0-0}
030·8	mw	G_0^{1-1}	964·3	vw		430·6	m	
043	w	$G_0^{1'-1'}$	975·7	w	$U_1^{1'-1'}$	438	m	
060·2	w		993·2	w		450	mw	$X_1'^{0-0}$
087·4	vw	$U_0^{1'-1'}$	40037·2	mw	$G_1'^{0-0}$	460·3	mw	X_1^{0-0}
106·7	vw		048·4	mw		592·9	w	R_2^{0-0}
122	vw	P_0^{0-0}	059·2	mw	L_0^{0-0}	702·3	w	S_2^{0-0}
138·9	mw	$G_0'^{0-0}$	075·7	mw	G_1^{0-0}	773	ew	$U_2^{1'-1'}$
148·0	mw		095·1	mw		861·7	w	$Y_0''^{0-0}$
185·2	mw	G_0^{0-0}	106·3	mw		911·5	mw	U_2^{0-0}
206·2	mw		123·5	mw	U_1^{0-0}	42070	vw	C_4^{1-1}
230·1	w	U_0^{0-0}	135	vw	$C_2^{11'-11'}$	080·5	ew	$C_4^{1'-1'}$
241·1	vw		162·4	vw	$C_2^{2'-2'}$	097·1	ew	
259·2	vw	$C_1^{2'-2'}$	242	mw	$A_2^{2'-2'}$	155	w	$A_4^{1'-1'}$
323·2	mw	$A_1^{11'-11'}$	252·9	mw	$E_1^{2'-2'}$	167	mw	
329·1	mw	$A_1^{2'-2'}$	274	mw	C_2^{1-1}	181·2	mw	$E_3^{1'-1'}$
342·0	mw		291·0	mw		190	mw	
350·6	w	$E_0^{11'-11'}$	300·4	mw	$C_2^{1'-1'}$	204	w	$X_2'^{1'-1'}$
364	vw	$K_1'^{0-0}$	318·4	ew	B_3^{0-0}	214	w	
379·5	mw	C_1^{1-1}	338·4	mw	A_2^{1-1}	234	ew	C_4^{0-0}
391·4	vw		352·7	m		305·3	ms	A_4^{0-0}
400·5	mw	$C_1^{1'-1'}$	376·7	ms	$A_2^{1'-1'}$	316·5	ms	E_3^{0-0}
412·5	mw	M_1^{0-0}	390·8	ms	$E_1^{1'-1'}$	346	m	$X_3'^{0-0}$
421·0	vw	B_2^{0-0}	400·0	m		749	w	$Y_1''^{0-0}$
430	vw	Q_0^{0-0}	430·1	mw	C_2^{0-0}	804	w	U_4^{0-0}
446	mw	A_0^{1-1}	440·8	mw		820	w	
459	m		446·8	ew	$L_1'^{0-0}$	43080	mw	$E_4^{1'-1'}$
474·0	ms	$A_1^{1'-1'}$	457·6	w	K_1^{0-0}	101	mw	$X_3^{1'-1'}$
483·3	ms		501·5	s	A_2^{0-0}	131	ew	C_5^{0-0}
490·1	m	$E_0^{1'-1'}$	517·5	s		192	m	A_5^{0-0}
495·3	mw	k_1^{0-0}	525	s	E_1^{0-0}	201	m	
500·5	m	$E_0^{1'-1'}$	540·1	ms				
518·3	w	W_0^{0-0}	552·0	mw	$X_0'^{0-0}$			

Note: The notation by which quantum numbers are expressed in the assignment column of this Table is the same as that used in Table I of Part VIII, and is explained in the Note beneath that Table (p. 464).

TABLE II.

Absorption Spectrum of 1 : 2 : 4 : 5-*Tetradeuterobenzene. Key to Assignments* (*cf. Table I*).

	Freq. (cm.$^{-1}$).	*p'*.	*p''*.	*s*.	*t*.	*u*.	*v*.
A	$= 38219 + \begin{Bmatrix}509{\cdot}5\\505\end{Bmatrix} + 895p' - 961p'' - 150s - 141t$	0—5	0, 1	0—2	0—3		
B	$= \quad " \quad - \begin{Bmatrix}591\\586\end{Bmatrix} + 895p' - 961p'' - 150s - 141t$	0—3	0, 1	0—2	0—3		
C	$= \quad " \quad + \begin{Bmatrix}509{\cdot}5\\505\end{Bmatrix} + \begin{Bmatrix}509{\cdot}5 - 591\\505 - 586\end{Bmatrix} + 895p' - 961p'' - 150s - 141t$	0—5	0, 1	0, 1	0—2		
D	$= \quad " \quad + \begin{Bmatrix}509{\cdot}5 - 591\\505 - 586\end{Bmatrix} - \begin{Bmatrix}509{\cdot}5\\505\end{Bmatrix} - 150s - 141t$			0, 1	0, 1		
E	$= \quad " \quad + 1414 + 895p' - 150s - 141t$	0—4		0, 1	0—2		
G	$= \quad " \quad + \begin{Bmatrix}509{\cdot}5\\505\end{Bmatrix} + 2 \times 233 + 895p' - 150s - 141t$	0—2		0, 1	0—2		
G'	$= \quad " \quad + \begin{Bmatrix}509{\cdot}5\\505\end{Bmatrix} + 2 \times 208 + 895p' - 150s - 141t$	0, 1		0, 1	0—2		
H	$= \quad " \quad - \begin{Bmatrix}591\\586\end{Bmatrix} + 2 \times 233$						
J	$= \quad " \quad - 150s - 141t - 175u - 116v$			0—2	0—3	0—2	0, 1
j	$= \quad " \quad + \begin{Bmatrix}509{\cdot}5\\505\end{Bmatrix} - \begin{Bmatrix}591\\586\end{Bmatrix} - 150s - 141t - 175u$			0, 1	0, 1	0, 1	
K	$= \quad " \quad + \begin{Bmatrix}509{\cdot}5\\505\end{Bmatrix} + 2 \times 419 + 895p'$	0, 1					
K'	$= \quad " \quad - \begin{Bmatrix}591\\586\end{Bmatrix} + 2 \times 419 + 895p'$	0, 1					
k	$= \quad " \quad + \begin{Bmatrix}509{\cdot}5\\505\end{Bmatrix} - 128 + 895p'$	0, 1					
k'	$= \quad " \quad - \begin{Bmatrix}591\\586\end{Bmatrix} - 128$						
κ	$= \quad " \quad + \begin{Bmatrix}509{\cdot}5\\505\end{Bmatrix} + 419 - 383$						
L	$= \quad " \quad + \begin{Bmatrix}509{\cdot}5\\505\end{Bmatrix} + 2 \times 665$						
L'	$= \quad " \quad + 2 \times 665 \times 895p'$	0, 1					
M	$= \quad " \quad + \begin{Bmatrix}509{\cdot}5\\505\end{Bmatrix} - 210 + 895p'$	0, 1					
N	$= \quad " \quad - \begin{Bmatrix}591\\586\end{Bmatrix} - 210 - 150s - 141t$			0, 1	0, 1		
P	$= \quad " \quad + 2 \times 452$						
Q	$= \quad " \quad + \begin{Bmatrix}509{\cdot}5\\505\end{Bmatrix} + 2 \times 351$						
R	$= \quad " \quad + \begin{Bmatrix}509{\cdot}5\\505\end{Bmatrix} + 2 \times 535 + 895p'$	0—2					
S	$= \quad " \quad + \begin{Bmatrix}509{\cdot}5\\505\end{Bmatrix} + 2 \times 591 + 895p'$	0—2					
T	$= \quad " \quad - \begin{Bmatrix}591\\586\end{Bmatrix} + 2 \times 591 + 895p'$	0, 1					
U	$= \quad " \quad - \begin{Bmatrix}509{\cdot}5\\505\end{Bmatrix} + \begin{Bmatrix}509{\cdot}5\\505\end{Bmatrix} + 895p' - 141t$	0—4			0, 1		
V	$= \quad " \quad + \begin{Bmatrix}509{\cdot}5\\505\end{Bmatrix} + 2 \times 509{\cdot}5 + 895p'$	0, 1					
W	$= \quad " \quad + 2 \times 649$						
X	$= \quad " \quad + 2355 + 895p'$	0, 1					
X'	$= \quad " \quad + 2333 + 895p' - 141t$	0—3			0, 1		
Y''	$= \quad " \quad + \begin{Bmatrix}509{\cdot}5\\505\end{Bmatrix} + 3133 + 895p'$	0, 1					

Note: The frequency 38219 cm.$^{-1}$ is that of the electronic origin. The other frequencies are vibration frequencies, which are assigned to vibrations in Table III. The frequencies in braces are to be read alternatively. The symbols for quantum numbers are those used in Table II of Part VIII, and are defined in the Note beneath Table I of Part VIII (p. 464).

the vibrations will be made clear by reference to Part I, Section 7, and especially to Table V of that section (p. 415) (for diagrams of the vibrations, see *J.*, 1946, pp. 278—299).

The naming of the band series has been made to agree as far as possible with that used for the absorption spectrum of 1 : 4-dideuterobenzene : series A—E, G, G', H, H', J, j, K, L, M, N, P, Q, R, U, W, X, X', and Y'' correspond in the two spectra. Series A—E, G, H, J, M, and N correspond to the identically named series of all the absorption spectra of all the benzenes studied.

TABLE III.

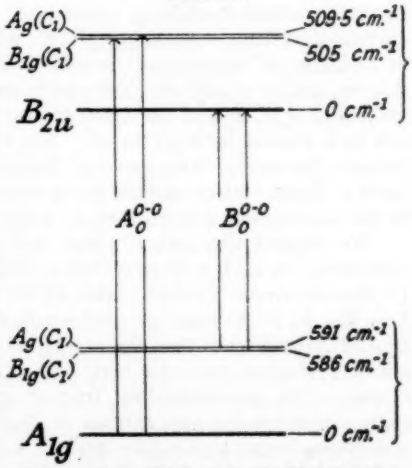
Absorption Spectrum of 1 : 2 : 4 : 5-*Tetradeuterobenzene. Assignment to Vibrations of the Vibration Frequencies (cm.$^{-1}$) contained in Table II.*

Upper-state fundamental frequencies (+).	Lower-state fundamental frequencies (−).	Diffs. of upper- and lower-state fundamentals (−).	Vibration.
895	961	—	A_g(C)
509·5	591	81	A_g(C 1)
1414	—	—	A_g(C 2)
3133	—	—	A_g(H 1)
2355	—	—	A_g(H 2)
208	—	141	A_u(C)
591	—	—	A_u(H)
505	586	81	B_{1g}(C 1)
1414	—	—	B_{1g}(C 2)
2333	—	—	B_{1g}(H 2)
233	383	150 } +(36)	B_{1u}(C)
419	—	128 }	B_{1u}(H 1)
665	—	—	B_{1u}(H 2)
452	—	210	B_{2g}(H)
351	—	—	B_{2g}(C)
649	—	—	B_{2g}(H 1)
535	—	—	B_{2g}(H 2)

Note: By the addition of one quantum of the A_u(C) vibration to one state, and one of the B_{1u}(C) vibration to the other, difference frequencies of 175 cm.$^{-1}$ and 116 cm.$^{-1}$ arise, which appear explicitly in equations J and j of Table II.

(2) *Band Series* A—D, U, *and* V.—Series A—D, as usual, provide the main framework of the spectrum (cf. Part I, Section 4). As with 1 : 4-dideuterobenzene, they arise from one-quantum changes in *both* of the similar vibrations A_g(C 1) and B_{1g}(C 1), with the result that the bands of all four series are close doublets. The scheme of transitions for the two simplest active origins, A_0^{0-0} and B_0^{0-0}, is illustrated in Fig. 2. The reason why the origins C_0^{0-0} and D_0^{0-0} also appear as doublets, and not as higher multiplets, corresponding to the increase in the number of split levels with advancing quantum number, is doubtless the same as for 1 : 4-dideuterobenzene (Part VIII, Section 2).

FIG. 2.



Term scheme illustrating doublet structure of A and B bands. (Not to scale.)

The doublet separations of the fundamental vibrational levels, as given by the frequencies of the band maxima, are 4·5 cm.$^{-1}$ in the excited state and 5·0 cm.$^{-1}$ in the ground state—a little less, therefore, than for 1 : 4-dideuterobenzene, for which it is 5·5 cm.$^{-1}$ in either state. With reference to the ground state, Poole also obtained a somewhat smaller separation with 1 : 2 : 4 : 5-tetradeuterobenzene than with 1 : 4-dideuterobenzene, 3·2 cm.$^{-1}$ as against 4·3 cm.$^{-1}$, by resolution of the Raman doublets, although (as he appreciated) his individual separations were rendered low by the overlapping of rounded Raman bands (*J.*, 1946, 245, 276).

As regards the ground state, Herzfeld, Ingold, and Poole assigned the uppermost of the split fundamental levels to the A_g(C 1) vibration (*J.*, 1946, 272). Part of their argument applies equally to the excited state, and suggests that here also the upper level belongs to the vibration A_g(C 1), and the lower to the vibration B_{1g}(C 1). Confirmation can, perhaps, be seen in the circumstance that the upper frequency appears to have a greater tendency than has the other to repeat itself in such a progression (characteristic of totally symmetrical vibrations) as that constituted by the three bands A_0^{0-0}, U_0^{0-0}, and V_0^{0-0}, or by other corresponding bands of these three series.

Series U involves the excitation of two upper-state quanta of the vibrations with which we are dealing, and series V the excitation of three such quanta, in transitions which in either case start from ground levels containing no such quanta. The persistence of series U is notable: a

series U is present in the absorption spectrum of 1 : 4-dideuterobenzene, but it is much less extensively developed. On the other hand, a closely corresponding series U is strongly developed in the absorption spectrum of benzene.

In all the series under discussion, progressions in the breathing frequency, A_g(C), 895 cm.$^{-1}$ in the upper electronic state and 961 cm.$^{-1}$ in the lower state, follow the usual lines, except for maintaining the doublet structures of the four active origins.

As in the spectrum of 1 : 4-dideuterobenzene, so also in the present spectrum, series A—D involve two sequence intervals, which combine to give "simply branching" sequences (Part VIII, Section 1). The intervals are 141 cm.$^{-1}$ and 150 cm.$^{-1}$, but the latter value increases somewhat in the second quantum group, indicating some unelucidated disturbance to an overtone level.

The lower sequence interval is the same as the sequence interval of hexadeuterobenzene, and this identifies the 1 : 2 : 4 : 5-tetradeuterobenzene vibration as A_u''(C), the normal co-ordinate of which is identical with one normal co-ordinate of the sequence-forming vibration, E_u^+(C), of hexadeuterobenzene (Bailey, Carson, Gordon, and Ingold, *J.*, 1946, 298; cf. their diagram XIV, p. 299). The higher sequence interval must, therefore, belong to the vibration B_{1u}(C).

The series discussed determine the position of the electronic origin,

$$J_0^{0-0} = 38219 \pm 1 \text{ cm.}^{-1}$$

and the following fundamental frequencies:

A_g(C 1)$_{ground}$ = 591 cm.$^{-1}$	A_g(C 1)$_{excited}$ = 509·5 cm.$^{-1}$
B_{1g}(C 1)$_{ground}$ = 586 cm.$^{-1}$	B_{1g}(C 1)$_{excited}$ = 505 cm.$^{-1}$
A_g(C)$_{ground}$ = 961 cm.$^{-1}$	A_g(C)$_{excited}$ = 895 cm.$^{-1}$

The ground-state frequencies as found in the Raman spectrum of liquid 1 : 2 : 4 : 5-tetradeuterobenzene are as follows: A_g(C 1) = 589·0 cm.$^{-1}$, B_{1g}(C 1) = 585·8 cm.$^{-1}$, A_g(C) = 960·9 cm.$^{-1}$ (Herzfeld, Hobden, Ingold, and Poole, *J.*, 1946, 272).

(3) *Band Series* E.—The main point for discussion concerning this series is whether the spectrum contains one such series or two. On theoretical grounds we expect two, because two distinct carbon-stretching vibrations, A_g(C 2) and B_{1g}(C 2), take the place of the degenerate carbon-stretching vibration E_g^+(C 2), which is responsible for series E in the absorption spectrum of benzene or hexadeuterobenzene. Now the E bands of the present spectrum are at least double, and it would obviously be possible to assign one member of each pair of maxima to the vibration A_g(C 2) and the other to the vibration B_{1g}(C 2). However, we think that this might not be a correct interpretation. For all the E bands we have seen in the absorption spectra of isotopic benzenes, even those of benzene, 1 : 3 : 5-trideuterobenzene, and hexadeuterobenzene, have a characteristic double-band form; and when the E series clearly occurs in duplicate, as in the absorption spectrum of 1 : 4-dideuterobenzene, groups of four intensity maxima appear.

We suspect that two E series of 1 : 2 : 4 : 5-tetradeuterobenzene exist, but are accidentally coincident to such a degree that a clear resolution of such broad bands has not been possible. In the electronic ground state, as we know from Raman spectra, the separations, in mono-, 1 : 4-di-, 1 : 2 : 4 : 5-tetra-, and penta-deuterobenzene, of the split frequencies derived from the E_g^+(C 2) vibration of benzene are 17, 18, 8, and 5 cm.$^{-1}$ respectively. In the last case the corresponding Raman line can just, but only just, be resolved (unpublished observation by H. G. Poole). The corresponding frequency separations in the upper electronic state should be represented by the separations of duplicate E series. Now we find duplicate E series in the absorption spectra of mono- and 1 : 4-di-deuterobenzene (Parts X and VIII), with separations of 24 and 20 cm.$^{-1}$—of the same order as the already mentioned separations in the ground state. If, for the E_g^+(C 2)-derived vibrations of all these compounds, the frequency separations in the excited state should roughly follow the pattern of those in the ground state, the separations of duplicate E series in 1 : 2 : 4 : 5-tetra- and in penta-deuterobenzene would not improbably prove too small for observation by definite resolutions of the bands. Actually we are able to record a bare resolution of one of the E bands in the absorption spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene, but we could not repeat it for all the bands. The apparent separation of the resolved band, 3·5 cm.$^{-1}$, is, of course, likely to be rendered too low by the built-up intensity between the theoretical maxima. We have not yet seen the absorption spectrum of pentadeuterobenzene, but expect a similar difficulty in distinguishing duplicate E series there.

Taking, as for other E series, the lower-frequency maxima of the double bands as the better approximation to their vibrational origins, we assume the following as the best available values for the involved fundamental frequencies:

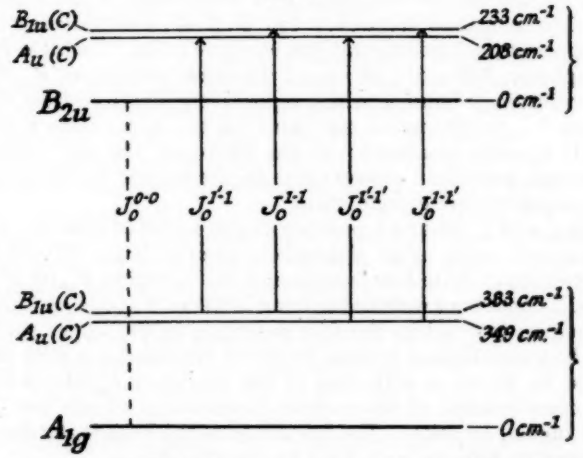
$$A_g(\text{C 2})_{excited} = 1414 \text{ cm.}^{-1} \qquad B_{1g}(\text{C 2})_{excited} = 1414 \text{ cm.}^{-1}$$

The ground-state frequencies, as given in the Raman spectrum of liquid 1 : 2 : 4 : 5-tetradeuterobenzene, are A_g(C 2) = 1572·1 cm.$^{-1}$ and B_{1g}(C 2) = 1564 cm.$^{-1}$ (*idem, ibid.*).

(4) *Band Series* G, G′, H, J, *and* j.—These series resemble the similarly named series of the absorption spectrum of 1 : 4-dideuterobenzene. Series G and G′ are duplicate series, the former depending on upward 0—2, 1—3, ..., transitions of the vibration B_{1u}(C), and the latter on similar transitions of the vibration A_u(C), in combination, in each case, with the electronic and vibrational transitions of series A. Of the two possible series H and H′, analogously dependent on transitions of the vibrations B_{1u}(C) and A_u(C) respectively, but in combination with the transitions of series B rather than of series A, we can discern clearly only the parent band of series H, the rest of the series and the whole of the duplicate series H′ being presumably obscured under the nearly continuous array of bands which in this spectrum, as in the absorption spectrum of 1 : 4-dideuterobenzene, constitute series J.

Just as in the spectrum of 1 : 4-dideuterobenzene, so also in the present spectrum, series J involves transitions between vibrating ground and electronically excited states containing the same *total* numbers of quanta of the vibrations B_{1u}(C) and A_u(C), but no other non-totally symmetrical quanta. Thus the series presents a " complex branching " sequence of many

FIG. 3.



$J_0^{1'-1} - J_0^{0-0} = 175$ cm.$^{-1}$. $J_0^{1'-1'} - J_0^{0-0} = 141$ cm.$^{-1}$.
$J_0^{1-1} - J_0^{0-0} = 150$ cm.$^{-1}$. $J_0^{1-1'} - J_0^{0-0} = 116$ cm.$^{-1}$.

Term scheme illustrating the development of series J. (*Not to scale.*)

weak bands. The one-quantum transitions are illustrated in Fig. 3; the 0—0 transition is, of course, forbidden. Again as in the spectrum of 1 : 4-dideuterobenzene, series j presents a less fully developed " complex branching " sequence, the transitions of which correspond to those of series J, but have additionally in each of the combining states one quantum of either the vibration A_g(C 1) or the vibration B_{1g}(C 1). Here the 0—0 transition, though theoretically allowed on account of the presence of the last-named vibrations, is too weak to produce an observed band.

The series discussed in this Section, together with the sequence belonging to the series considered in Section 2, enable us to fix the fundamental frequencies of the vibrations A_u(C) and B_{1u}(C) in both the lower and the upper electronic states :

$A_u(C)_{ground} = 349$ cm.$^{-1}$ $A_u(C)_{excited} = 208$ cm.$^{-1}$
$B_{1u}(C)_{ground} = 383$ cm.$^{-1}$ $B_{1u}(C)_{excited} = 233$ cm.$^{-1}$

The assignment of the lower frequency in each state to the A_u(C) vibration is determined by the identity of the frequencies with those found for the E_u^+(C) vibration of hexadeuterobenzene (Part IV, Section 3); for these vibrations must of principle have identical frequencies in each state (cf. Section 2). Considerations based on the forms of the normal co-ordinates would also lead us to assign the lower frequency in each state to the A_u(C) vibration, in which the hydrogen motion is wholly concentrated in the deuterium atoms (Bailey, Carson, Gordon and Ingold, *loc. cit.*). The ground-state frequencies are subject to an independent check. For the A_u(C) frequency has been indirectly estimated from higher harmonics of Raman and infra-red spectra

as 352 cm.$^{-1}$ (Herzfeld, Ingold, and Poole, *J.*, 1946, 316); and it has been directly observed as 350 cm.$^{-1}$ in the form of the E_u^+ fundamental in the Raman spectrum of liquid hexadeuterobenzene (Poole, *J.*, 1946, 245); whilst the B_{1u}(C) fundamental band has been found, at 383 cm.$^{-1}$, in the infra-red spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene vapour (Bailey, Carson, Gordon, and Ingold, *loc. cit.*).

(5) *Band Series* K, K′, k, k′, κ, L, L′, S, *and* T.—According to our assignments, all these series are connected in various ways with one or other of the three hydrogen vibrations of the B_{1u} and A_u classes. Progressions K and K′ commence with bands situated 837 cm.$^{-1}$ above A_0^{0-0} and B_0^{0-0}, respectively. Partly from reasons based on comparisons with absorption spectra of other benzenes (Part XI), and partly on the internal evidence of this spectrum, we assign the interval 837 cm.$^{-1}$ as the first overtone, in the upper electronic state, of the vibration B_{1u}(H 1), the nearest analogue this molecule can produce of the hexagonal out-of-plane, hydrogen-bending vibration, A_{2u}(H), of benzene or hexadeuterobenzene. Support is found in the series k and k′, which consist of bands displaced by 128 cm.$^{-1}$ below the stronger bands of series A and B, respectively. We regard them as arising from 1—1 transitions of the vibration B_{1u}(H 1), in combination with the transitions of the related A or B bands. Similar bands, for which the displacement is 114 cm.$^{-1}$, in the absorption spectrum of hexadeuterobenzene were attributed (Part IV, Section 5) to analogously combined 1—1 transitions of the allied vibration, A_{2u}(H), of that molecule. The overtone frequency for 1 : 2 : 4 : 5-tetradeuterobenzene, 837 cm.$^{-1}$, corresponds to an upper-state fundamental frequency, 419 cm.$^{-1}$, which, in combination with the fundamental frequency, 383 cm.$^{-1}$, of one of the other vibrations, B_{1u}(C), of the symmetry class B_{1u} accounts for the single band, κ, which is positively displaced from the main origin, A_0^{0-0}, by the interval 34 cm.$^{-1}$. Furthermore, our value for the upper-state fundamental frequency of the vibration B_{1u}(H 1), when combined with the difference, 128 cm.$^{-1}$, between the lower- and upper-state fundamentals, provides a correct value for the already known fundamental frequency of this vibration in the electronic ground state.

The bands of series L and L′ involve a positive displacement of 1330 cm.$^{-1}$ from A_0^{0-0} and J_0^{0-0}, respectively. Comparisons with other absorption spectra (Part XI) lead us to assign the common interval as the upper-state first overtone of the vibration B_{1u}(H 2).

Progressions S and T commence with bands lying 1183 cm.$^{-1}$ above A_0^{0-0} and B_0^{0-0} respectively. We interpret the common interval as the first overtone, in the upper electronic state, of the vibration A_u(H). The identification follows from the circumstance that the frequency of the vibration A_u(H) must be identical with that of the vibration E_u^+(H) of hexadeuterobenzene. This follows from a consideration of the normal co-ordinates of the two vibrations (Bailey, Carson, Gordon, and Ingold, *loc. cit.*). The frequency of the hexadeuterobenzene vibration has already been determined as 590 cm.$^{-1}$ (cf. Part IV, Section 10).

The above assignments lead to the following fundamental frequencies :

$$B_{1u}(\text{H 1})_{\text{ground}} = 547 \text{ cm.}^{-1} \qquad B_{1u}(\text{H 1})_{\text{excited}} = 419 \text{ cm.}^{-1}$$
$$B_{1u}(\text{H 2})_{\text{excited}} = 665 \text{ cm.}^{-1} \qquad A_u(\text{H})_{\text{excited}} = 591 \text{ cm.}^{-1}$$

The ground-state fundamental frequencies of two of these vibrations have been observed in the infra-red spectrum (*idem, ibid.*) : B_{1u}(H 1) = 548 cm.$^{-1}$, B_{1u}(H 2) = 925 cm.$^{-1}$. The remaining ground-state frequency has been indirectly estimated, largely from Raman and infra-red combinations tones : A_u(H) = 793 cm.$^{-1}$ (Herzfeld, Ingold, and Poole, *loc. cit.*).

(6) *Band Series* M, N, *and* P.—Series M and N consist of bands negatively displaced from the stronger bands of series A and B, respectively, by the common interval 210 cm.$^{-1}$. They are interpreted as involving, in combination with the transitions of series A or B, 1—1 transitions of the vibration, B_{2g}(H). This vibration is identical with one form of the degenerate vibration, E_g^-(H), of hexadeuterobenzene, and is therefore identical in frequency with that vibration (Herzfeld, Hobden, Ingold, and Poole, *J.*, 1946, 285; cf. their diagram XII). In the absorption and in the fluorescence spectra of hexadeuterobenzene we find series, also called M and N, consisting of bands displaced from A or B bands by the identical interval, and these have been interpreted as involving 1—1 transitions of the vibration E_g^-(H). Our assignment of the 1 : 2 : 4 : 5-tetradeuterobenzene series follows from this comparison. We recognise in the appearance of the single band P_0^{0-0} the excitation, in the upper electronic state, of the first overtone of the vibration B_{2g}(H). These assignments lead to the following fundamental frequencies :

$$B_{2g}(\text{H})_{\text{ground}} = 662 \text{ cm.}^{-1} \qquad B_{2g}(\text{H})_{\text{excited}} = 452 \text{ cm.}^{-1}$$

The ground-state value, derived from the Raman spectrum of liquid 1 : 2 : 4 : 5-tetradeuterobenzene, is 663·6 cm.$^{-1}$ (*idem, J.*, 1946, 272).

(7) *Band Series* Q, R, *and* W.—These series are connected with the three vibrations of the symmetry class B_{2g}. They are assigned essentially on the basis of comparisons of the frequencies with those of other benzenes (Part XI). The single band Q_0^{0-0}, situated 702 cm.$^{-1}$ above A_0^{0-0}, is explained as an excitation of the first overtone of the vibration B_{2g}(C) in the upper electronic state, in combination with the electronic and vibrational transitions of A_0^{0-0}. The prominent band, R_0^{0-0}, the parent of progression R, lies 1070 cm.$^{-1}$ above A_0^{0-0}, and is interpreted as an analogously combined excitation of the first overtone of the vibration B_{2g}(H 2). Band W_0^{0-0} lies 1299 cm.$^{-1}$ above the electronic origin, and is explained by the assumption of a transition from the " vibrationless " ground state to the two-quantum level of the vibration B_{2g}(H 1) in the excited state. These assignments lead to the following fundamental frequencies:

$$B_{2g}(\mathrm{C})_{\mathrm{excited}} = 351 \text{ cm.}^{-1} \qquad B_{2g}(\mathrm{H\ 1})_{\mathrm{excited}} = 649 \text{ cm.}^{-1}$$
$$B_{2g}(\mathrm{H\ 2})_{\mathrm{excited}} = 535 \text{ cm.}^{-1}$$

The corresponding ground-state frequencies, as found in the Raman spectrum of liquid 1 : 2 : 4 : 5-tetradeuterobenzene are as follows: B_{2g}(C) = 615·1 cm.$^{-1}$, B_{2g}(H 1) = 929·7 cm.$^{-1}$, B_{2g}(H 2) = 767·1 cm.$^{-1}$ (*idem*, *J.*, 1946, 272).

(8) *Band Series* X, X′, *and* Y″.—Just above the strong band-group A_2^{0-0}—E_1^{0-0} lie two sharp and conspicuous bands, displaced by 2333 cm.$^{-1}$ and 2355 cm.$^{-1}$ from the electronic origin. They are the parent bands of series X′ and X, respectively. They probably gain some of their intensity by resonance with the neighbouring A and E bands; and especially is this likely to be true of the nearer band $X_0'^{0-0}$, which starts a more extensive progression than its neighbour X_0^{0-0}. These series are obviously connected with the two deuterium-stretching vibrations—those of the A_g and B_{1g} classes—one-quantum excitations of which are allowed in the spectrum. The parent bands are explained by transitions from the " vibrationless " level of the electronic ground state to the fundamental levels of the vibrations in the excited state. The two vibrations thus have the upper-state fundamental frequencies 2333 cm.$^{-1}$ and 2355 cm.$^{-1}$. We may reach a decision as to which belongs to the A_g and which to the B_{1g} vibration by an argument quite similar to that employed in connexion with the two analogous protium-stretching vibrations of 1 : 4-dideuterobenzene (Part VIII, Section 8). From a consideration of the normal co-ordinates, we expect the frequency of the B_{1g}(H 2) vibration of 1 : 2 : 4 : 5-tetradeuterobenzene to lie very close to that of the E_g^+(H 1) vibration of hexadeuterobenzene. The latter has the frequency 2320 cm.$^{-1}$ (cf. Part IV); and therefore we assign to the B_{1g}(H 2) vibration of 1 : 2 : 4 : 5-tetradeuterobenzene the lower of the two observed frequencies, 2333 cm.$^{-1}$, recognising that it may have been raised a few wave-numbers above its unperturbed value by the resonance already mentioned.

Progression Y″ starts with a band, $Y_0''^{0-0}$, which is strikingly sharp for the part of the spectrum in which it appears. It lies 3133 cm.$^{-1}$ above A_0^{0-0}, and this interval we take to represent the fundamental frequency of the single protium-stretching vibration, A_g(H 1), one-quantum excitations of which are allowed in the spectrum.

Thus we identify the following hydrogen-stretching fundamental frequencies of the excited state of 1 : 2 : 4 : 5-tetradeuterobenzene:

$$A_g(\mathrm{H\ 1})_{\mathrm{excited}} = 3133 \text{ cm.}^{-1} \qquad A_g(\mathrm{H\ 2})_{\mathrm{excited}} = 2355 \text{ cm.}^{-1}$$
$$B_{1g}(\mathrm{H\ 2})_{\mathrm{excited}} = 2333 \text{ cm.}^{-1}$$

The corresponding ground-state frequencies, as determined by Herzfeld, Hobden, Ingold, and Poole (*loc. cit.*) from the Raman spectrum of the liquid, are as follows: A_g(H 1) = 3045·0 cm.$^{-1}$, A_g(H 2) = 2285·0 cm.$^{-1}$, B_{1g}(H 2) = 2272 cm.$^{-1}$. As usual, the frequencies of the hydrogen-stretching vibrations are higher in the excited state than in the ground state.

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104. *Excited States of Benzene. Part X. Analysis of the First Ultraviolet Band System of the Absorption Spectrum of Monodeuterobenzene.*

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The measurements of Beck and Sponer on the ultraviolet absorption spectrum of monodeuterobenzene are analysed as outlined in the abstract of Part I. A list of eighteen fundamental frequencies of the upper electronic state is given: all are assigned to their vibrations. Most of the basis of the assignment is given, but completion is reserved for Part XI.

(1) *Data.*—The first ultraviolet absorption system of monodeuterobenzene has been described by Beck and Sponer (*J. Chem. Physics*, 1942, **10**, 575). They assigned many of the bands, and we accept most of their assignments. It would hardly have been possible for them to proceed any further with the analysis of the spectrum on the basis of the knowledge that was then available of the frequencies of the electronic ground state. Having now a much more complete knowledge of these frequencies, as well as some useful experience in the interpretation of the somewhat simpler electronic band systems of more symmetrically substituted benzenes, we have attempted a substantially complete analysis of the spectrum.

The first two columns of Table I contain Beck and Sponer's frequency and intensity data, whilst the third column records our assignments according to a literal notation, the interpretation of which is contained in Tables II and III. The symbols have been made to correspond as closely as possible to those used in connection with the absorption spectra of other benzenes, especially 1 : 4-dideuterobenzene (Part VIII).

One general difference between Beck and Sponer's analysis and ours may be mentioned. They assumed certain of the weak bands to depend on an allowed electronic transition, implying a reduced electronic symmetry as a result of isotopic substitution. On the other hand, we

TABLE I.

Absorption Spectrum of Monodeuterobenzene. Frequencies, Intensities, and Assignments (cf. Tables II and III).

Freq. (cm.$^{-1}$).	Inty.	Assgnt.	Freq. (cm.$^{-1}$).	Inty.	Assgnt.	Freq. (cm.$^{-1}$).	Inty.	Assgnt.
37026	w	$R_0^{1'-1'}$	37788	3	$J_0^{11'-2'}$	38215	5	$N_1'^{0-0}$
041	w	$B_0^{2'-3'}$	796	3	$J_0^{2-11'}$	227	5	$C_0^{2'-2'}$
046	w	$B_0^{12'-12'}$	801	3	$J_0^{2'-2'}$	235	5br	$C_0^{11'-11'}$
119	2	$D_0^{11'-11'}$	820	3	J_0^{2-2}	256	5	$M_0'^{1'-1'}$
134	3	$N_0'^{1'-1'}$	828	3	$J_0^{2'-11'}$	275	5	$B_1^{1'-1'}$
185	4	R_0^{0-0}	844	2	$J_0^{11'-2}$	300·8	7	Q_0^{0-0}
201	4	$B_0^{2'-2'}$	851	2	$J_0^{2'-2}$	320·8	7	$A_0^{2'-2'}$
207	4	$B_0^{11'-11'}$	860	2	$j_0^{1-1'}$	326·8	7	$A_0^{11'-11'}$
226	w	$L_0^{1'-1'}$	884	2	j_0^{1-1}	335	7	A_0^{2-2}
256	4	N_0^{0-0}	896	4	$j_0^{1'-1}$	343	6L	$K_0^{1'-1'}$
270	3	$D_0^{1'-1'}$	914	2br	$h_0'^{0-0}$	352	5L	D_1^{0-0}
275	4		948	4	$J_0^{1-1'}$	374·5	7	M_0^{0-0}
280	4	D_0^{1-1}	961	4	$J_0^{1'-1'}$	395	7br	$C_0^{1'-1'}$
295	4	$N_0''^{0-0}$	969	3	J_0^{1-1}	399	6	C_0^{1-1}
328	4	i_0''	971	4		413·2	7	$M_0'^{0-0}$
346	4	i_0'	975	2	H_0^{0-0}	421·8	7	k_0^{0-0}
360·7	6	$B_0^{1'-1'}$	982	4	$J_0^{1'-1}$	433·7	6	B_1^{0-0}
367·8	6	B_0^{1-1}	997	4	$H_0'^{0-0}$	443·0	7	
375	1		38006	4		480·1	8	$A_0^{1'-1'}$
381	1	L_0^{0-0}	013	3	$A_0^{22'-22'}$	487·8	8	A_0^{1-1}
387	4		020	2	$A_0^{31'-31'}$	496	5	K_0^{0-0}
433·5	6	D_0^{0-0}	036	4	j_0^{0-0}	504·1	7	
442	2		059	5br	$M_0^{1'-1'}$	554·7	8	C_0^{0-0}
454	2	B_{1-1}^{0-0}	108	3	R_1^{0-0}	583	6	A_{1-1}^{0-0}; I_0
520	7	B_0^{0-0}	114	5	$B_1^{2'-2'}$	598	7	I_0''
529	5	w_{-1}	118	—		640·8	10	A_0^{0-0}
564	2br	v_0''	123	—	$B_1^{11'-11'}$	688	4	P_0^{0-0}
578	4	C_{-1}^{0-0}	125	vw		733	4	J_1^{2-2}
604	2	v_0'	130	4	B_1^{2-2}	799	4	$G_0'^{2'-2'}$
630	4	v_0	142	4	$Q_0^{1'-1'}$	869	4br	$J_1^{1-1'}$
636	3		156	4	Q_0^{1-1}	891	4	J_1^{1-1}
659	6	A_{-1}^{0-0}	161	w	$A_0^{3'-3'}$	913	4	$H_1'^{0-0}$
668	2br	J_0^{3-3}	165	5	$A_0^{12'-12'}$	938	6	G_0^{1-1}
677	2	$J_0^{12'-21'}$	174	5	$A_0^{21'-21'}$	958	6	$G_0'^{1'-1'}$
700	3	$j_0^{11'-2'}$	183	5	A_0^{3-3}	963	4	$G_0'^{1-1}$
739	3	$j_0^{2'-11'}$	196	5	D_1^{1-1}	39022	5	R_2^{0-0}
767	3	$J_0^{2-2'}$	210	5	$M_0^{1'-1'}$	059	6	$Q_1^{1'-1'}$

TABLE I—*contd.*

Freq. (cm.$^{-1}$).	Inty.	Assgnt.	Freq. (cm.$^{-1}$).	Inty.	Assgnt.	Freq. (cm.$^{-1}$).	Inty.	Assgnt.
39068	5	Q_1^{1-1}	39592	—	K_0'	40472·5	8	A_2^{0-0}
077	w	$A_1^{3'-3'}$	595·7	7	$E_0'^{0-0}$	480·7	8	
090·6	6	G_0^{0-0}	622	7		489·6	8	E_1^{0-0}
116·7	7	$G_0'^{0-0}$	650	5br	$O_0^{1'-1'}$	506·6	7	$E_1'^{0-0}$
221	6	Q_1^{0-0}	675	5	U_0^{0-0}	520·6	7	
228	6	$A_1^{2'-2'}$	744	6	$O_0'^{0-0}$	597	6	U_1^{0-0}
241	6		788	3	$J_2^{1-1'}$	718	6	O_1^{0-0}
256	6L	A_1^{2-2}	808·0	7	O_0^{0-0}	729	6	
263	6L		867	5	$G_1'^{1'-1'}$	836	5	$T_1^{1'-1'}$
271	6L	$E_0^{2'-2'}$	878	4		918	6	$z_0^{1'-1'}$
288	6L		894	5	$G_1'^{1-1}$	949	6	$x_0'^{1'-1'}$
(307)	—	$C_1^{1'-1}$	917	5br	$T_0^{1'-1'}$	986	6	Y_0^{0-0}
331	L	$M_1'^{0-0}$	964	5	$z_0'^{0-0}$	998	6	T_1^{0-0}
343	6	k_1^{0-0}	40011	6L	G_1^{0-0}	41040	6br	$X_0'^{1-1'}$
364	7	B_2^{0-0}	019	7	S_0^{0-0}	083	6br	z_0^{0-0}
392·6	7	$A_1^{1'-1'}$	027	5	$G_1'^{0-0}$	111	6br	$x_0'^{0-0}$
401·4	7		039	6		164	6	$M_2'^{0-0}$
419·6	8	$E_0^{1'-1'}$	077	7	T_0^{0-0}	196	7	$X_0'^{0-0}$
437	5	$E_0'^{1'-1'}$	252	6L	$M_2'^{0-0}$	205	6	$X_0''^{0-0}$
466	7		288	6	B_3^{0-0}	393	7br	A_3^{0-0}
473	7	C_1^{0-0}	311	6br	$A_2^{1'-1'}$	408	6br	E_2^{0-0}
552·7	9	A_1^{0-0}	322	6		427	—	$E_2'^{0-0}$
561·1	9		340	6	E_1^{1-1}	770	6	$Y_0'''^{0-0}$
571	8	E_0^{0-0}	373	6L	$E_1'^{1-1}$	42108	—	$X_1'^{0-0}$
581·3	8		390	br	C_2^{0-0}	116	6	

Note: In this Table quantum numbers are indicated according to the conventions stated in the Note beneath Table I, Part VIII (p. 464), except that the sequence-forming vibration with the higher frequencies, identical with the vibration A_u(C) of 1 : 4-dideuterobenzene, is the A_2(C) vibration of monodeuterobenzene, whilst the sequence-forming vibration having the lower frequencies, approximately corresponding to the B_{1u}(C) vibration of 1 : 4-dideuterobenzene, is the B_2(C) vibration of monodeuterobenzene.

consider all the observed bands to depend on the forbidden electronic transition A_{1g}–B_{2u}, their spectral activity arising from deformation of the molecule by vibrations.

(2) *Band Series* A—D, U, v, v′, v″, *and* w.—As usual, band series A—D furnish the main spectral pattern. The parent bands A_0^{0-0}, B_0^{0-0}, C_0^{0-0}, and D_0^{0-0} arise from upward 0—1, 1—0, 1—2, and 2—1 transitions, respectively, of the main perturbing vibration, in combination with the electronic transition. These parent bands form the starting points of positive progressions in the ring-swelling vibration, and the bands of these progressions themselves form the starting points of negatively running sequences due to n—n transitions in certain out-of-plane vibrations of low frequencies. We also find in the spectrum a much weaker series called U, which is analogous to the similarly named series in the absorption spectrum of benzene, and depends upon upward 0—2 transitions of the perturbing vibration.

The fundamental frequencies of the main perturbing vibration, as given by the positions of the four parent bands of series A—D, are 603 cm.$^{-1}$ in the ground state and 517 cm.$^{-1}$ in the electronically excited state. Actually this vibration of monodeuterobenzene consists of the two planar, carbon-bending vibrations, A_1(C 1) and B_1(C 1), of nearly identical frequencies, and thus we might have expected the bands of the series A—D to appear as close doublets. In fact, in the absorption spectra of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene, a similar cause does lead to the appearance of close doublets in the corresponding band series. However, in the case of monodeuterobenzene, Beck and Sponer failed to obtain evidence of any such doublet character, and some photographs which we have taken of the same spectrum have yielded a like result. This appears the less remarkable when it is recalled that these two vibrations appear in the Raman spectrum as a single unresolved line at 601·8 cm.$^{-1}$ (Bailey *et al.*, *J.*, 1946, 299). Experience in the resolution of the corresponding Raman doublets of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene (Poole, *J.*, 1946, 245; cf. *ibid.*, p. 272) suggests that the separation of the monodeuterobenzene frequencies is unlikely to exceed 2 cm.$^{-1}$. From our study of some of the sharper bands of the ultraviolet absorption spectrum of monodeutero-

TABLE II.

Absorption Spectrum of Monodeuterobenzene. Key to Assignments (cf. Table I).

	Freq. (cm.$^{-1}$).	p'.	p''.	s.	t.	u.	v.
A	= 38124 + 517 + 920p' − 981p'' − 150s − 161t	0—3	0, 1	0—3	0—3		
B	= ,, − 603 + 920p' − 150s − 161t	0—3		0, 1	0—3		
C	= ,, + 2 × 517 − 603 + 920p' − 981p'' − 150s − 161t	0—2	0, 1	0—2	0, 1		
D	= ,, + 517 − 2 × 603 + 920p' − 150s − 161t	0, 1		0, 1	0, 1		
E	= ,, + 1446 + 920p' − 150s − 161t	0—2		0, 1	0—2		
E′	= ,, + 1472 + 920p' − 150s − 161t	0—2		0, 1	0, 1		
G	= ,, + 517 + 2 × 230 + 920p' − 150s	0, 1		0, 1			
G′	= ,, + 517 + 2 × 243 + 920p' − 150s − 161t	0, 1		0, 1	0—2		
H	= ,, − 603 + 2 × 230						
H′	= ,, − 603 + 2 × 243 + 920p'	0, 1					
h′	= ,, + 517 − 2 × 603 + 2 × 243						
I	= ,, + 2 × 230						
I′	= ,, + 230 + 243						
i′	= ,, − 380 − 404						
i″	= ,, − 2 × 404						
J	= ,, + 920p' − 150s − 161t − 137u − 174v	0, 1		0—3	0—2	0—2	0—2
j	= ,, − 150s − 161t − 137u − 174v			0, 1	0, 1	0, 1	0, 1
K	= ,, + 517 − 134 − 161t				0, 1		
k	= ,, + 2 × 517 − 603 − 134 + 920p'	0, 1					
K′	= ,, + 517 + 2 × 476						
L	= ,, − 603 − 134 − 161t				0, 1		
M	= ,, + 517 − 265 − 150s − 161t			0, 1	0, 1		
M′	= ,, + 517 − 226 + 920p' − 161t	0—3			0, 1		
N	= ,, − 603 − 265						
N′	= ,, − 603 − 226 + 920p' − 161t	0, 1			0, 1		
O	= ,, + 517 + 2 × 585 + 920p' − 161t	0, 1			0, 1		
O′	= ,, + 517 + 2 × 552						
P	= ,, − 603 + 2 × 585						
Q	= ,, + 517 − 338 + 920p' − 150s − 161t	0, 1		0, 1	0, 1		
R	= ,, − 603 − 338 + 920p' − 161t	0—2			0, 1		
S	= ,, + 517 + 2 × 690						
T	= ,, + 517 + 2 × 720 + 920p' − 161t	0, 1			0, 1		
U	= ,, + 2 × 517 + 920p'	0, 1					
v	= ,, + 517 − 1005						
v′	= ,, + 517 − 1037						
v″	= ,, + 517 − 1077						
w	= ,, − 603 + 990 − 981p''		1				
X′	= ,, + 3072 + 920p' − 161t	0, 1			0, 1		
x′	= ,, + 517 − 603 + 3072 − 161t				0, 1		
X″	= ,, + 3081						
Y	= ,, + 517 + 2348						
Y‴	= ,, + 517 + 3129						
z	= ,, + 517 + 2443 − 161t				0, 1		
z′	= ,, − 603 + 2443						

Note: The frequency 38124 cm.$^{-1}$ is that of the electronic origin. The other frequencies are assigned to vibrations in Table III and in the Note thereunder.

benzene we derive the impression that the actual separation is appreciably smaller than 2 cm.$^{-1}$. Furthermore, this absorption spectrum yields a similar result in relation to the upper electronic state: here, also, the separation of the corresponding doublet level is probably well within 2 cm.$^{-1}$. The similarity of these results might have been expected by analogy with 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene, for each of which the measured doublet separations in the two electronic states are closely similar.

According to the selection rules, any of the 21 planar vibrations of monodeuterobenzene could be progression-forming; but we should expect to find the greatest activity of this type shown by that vibration, A_1(C), which is most closely similar to the main progression-forming vibration of benzene. In fact, the positive progressions in the absorption spectrum of monodeuterobenzene are essentially simple, and are dominated by the single vibration A_1(C), which occurs up to several quanta of frequency 920 cm.$^{-1}$ in the electronic upper state, and with one quantum of frequency 981 cm.$^{-1}$ in the lower state. The tendency to form branching progressions, involving a series of quantum changes of more than one vibration, appears to be very much less developed than in the case of 1 : 3 : 5-trideuterobenzene (Part VI). On the other hand, in the single band w_{-1} we observe, in combination with the electronic and vibrational transitions of B_0^{0-0}, the replacement of a single quantum of the vibration A_1(C) in the electronic

TABLE III.

Absorption Spectrum of Monodeuterobenzene. Assignment to Vibrations of the Vibration Frequencies (cm.$^{-1}$) contained in Table II.

Upper-state fundamental frequencies (+).	Lower-state fundamental frequencies (−).	Diffs. of upper- and lower-state fundamentals (−).	Vibration.
920	981	61	A_1(C)
990	1005	—	A_1(C′)
517	603	86	A_1(C 1)
1472	—	—	A_1(C 2)
—	1037	—	A_1(H′)
2348	—	—	A_1(H 1)
3129	—	—	A_1(H 2)
3081	—	—	A_1(H′ 2)
517	603	86	B_1(C 1)
1446	—	—	B_1(C 2)
—	1077	—	B_1(H′)
3072	—	—	B_1(H 2)
243	404	161	A_2(C)
585	—	265	A_2(H′)
230	380	150	B_2(C)
—	—	338	B_2(C′)
476	—	134	B_2(H 1)
552	—	226	B_2(H′ 1)
690	—	—	B_2(H 2)
720	—	—	B_2(H′ 2)

Note: By the addition of one quantum of the A_2(C) vibration to one, and one of the B_2(C) vibration to the other, of the two combining states, differences of 137 cm.$^{-1}$ and 174 cm.$^{-1}$ may arise, which appear explicitly in equations J and j of Table II. Concerning the frequency 2443 cm.$^{-1}$, see text (Section 9). The difference frequency 338 cm.$^{-1}$, together with the ground-state fundamental frequency 698 cm.$^{-1}$, known from the infra-red spectrum, gives the value 360 cm.$^{-1}$ for the fundamental frequency of the vibration B_2(C′) in the upper electronic state (Section 7).

ground state by one quantum of the near-trigonal planar bending vibration A_1(C′), of frequency 990 cm.$^{-1}$, in the upper electronic state; and in the single band ν_0 we see, in combination with the electronic and vibrational transitions of A_0^{0-0}, the loss of a single ground-state quantum, of frequency 1005 cm.$^{-1}$, of the same vibration, A_1(C′) in the electronic ground state. These bands can be regarded as vestiges of positive and negative progressions in the vibration A_1(C′). The single bands ν_0' and ν_0'' are similar to ν_0 except that the place of the vibration A_1(C′) is taken by either of two other vibrations. These are the planar protium-bending vibrations A_1(H′) and B_1(H′), having the frequencies 1037 cm.$^{-1}$ and 1077 cm.$^{-1}$ in the electronic ground state.

Two out-of-plane vibrations, A_2(C) and B_2(C), are concerned in the formation of the sequences, which are associated with the main bands of progressions A—D. The elementary frequency intervals, representing the differences between the fundamental frequencies of these vibrations in the lower and the upper electronic states, are 161 cm.$^{-1}$ and 150 cm.$^{-1}$. It is significant that the larger difference is identical with the larger of the two corresponding differences of 1 : 4-dideuterobenzene, and with the single sequence interval of benzene. The vibration A_2(C) of monodeuterobenzene is identical with the vibration A_u(C) of 1 : 4-dideuterobenzene, and with one form of the degenerate vibration E_u^+(C) of benzene; for in these vibrations the atoms on the para-axis, which in the deuterated compounds contains the deuterium atoms, do not move. It follows that the interval 161 cm.$^{-1}$ belongs to the A_2(C) vibration, and that the interval 150 cm.$^{-1}$ belongs to the B_2(C) vibration. The sequences mentioned, like the corresponding sequences of 1 : 4-dideuterobenzene, are of the " simply branching " type (Part VIII, Section 2) : in all the recorded bands, each of the two sequence-forming vibrations is excited with the same number of quanta in the two electronic states.

From these bands we may learn the frequency of the electronic origin,

$$J_0^{0-0} = 38124 \pm 1 \text{ cm.}^{-1}$$

and the following fundamental vibration frequencies :

A_1(C 1)$_{\text{ground}}$ = 603 cm.$^{-1}$ A_1(C 1)$_{\text{excited}}$ = 517 cm.$^{-1}$
B_1(C 1)$_{\text{ground}}$ = 603 cm.$^{-1}$ B_1(C 1)$_{\text{excited}}$ = 517 cm.$^{-1}$
A_1(C)$_{\text{ground}}$ = 981 cm.$^{-1}$ A_1(C)$_{\text{excited}}$ = 920 cm.$^{-1}$
A_1(C′)$_{\text{ground}}$ = 1005 cm.$^{-1}$ A_1(C′)$_{\text{excited}}$ = 990 cm.$^{-1}$
A_1(H′)$_{\text{ground}}$ = 1037 cm.$^{-1}$ B_1(H′)$_{\text{ground}}$ = 1077 cm.$^{-1}$

Independent values for all of these ground-state frequencies have been obtained from the Raman spectrum of liquid monodeuterobenzene: A_1(C 1) = B_1(C 1) = 601·8 cm.$^{-1}$, A_1(C) = 980·0 cm.$^{-1}$, A_1(C′) = 1006·8 cm.$^{-1}$, A_1(H′) = 1031 cm.$^{-1}$, B_1(H′) = 1075 cm.$^{-1}$ (Bailey *et al.*, *loc. cit.*).

(3) *Band Series* E *and* E′.—These bands are very similar to the corresponding bands of 1 : 4-dideuterobenzene (Part VIII, Section 3). They are double bands, two of which, one belonging to the E and the other to the E′ series, lie just above each of the main bands of progression A, starting at the second member. We assume these bands to be formed in 0—1 transitions of the two carbon-stretching vibrations of similar frequencies, A_1(C 2) and B_1(C 2), in combination, in some cases, with the usual progression- and sequence-forming vibrations. Probably these bands gain much of their intensity by resonance with the neighbouring A bands, and they may also suffer upward displacements of frequency. For this reason we take, as heretofore, the lower of the frequencies of the two intensity maxima of each band as the better approximation to the unperturbed position of its vibrational origin.

The two parent bands, E_0^{0-0} and $E_0'^{0-0}$, lie 1446 cm.$^{-1}$ and 1472 cm.$^{-1}$, respectively, above the electronic origin. We connect these bands with the vibrations B_1(C 2) and A_1(C 2), respectively. The assignment is based on a consideration of normal co-ordinates closely similar to that employed in assigning the corresponding bands of 1 : 4-dideuterobenzene (Part VIII, Section 3). We thus derive the following fundamental frequencies :

$$A_1(\text{C 2})_{\text{excited}} = 1472 \text{ cm.}^{-1} \qquad B_1(\text{C 2})_{\text{excited}} = 1446 \text{ cm.}^{-1}$$

The corresponding ground-state frequencies, as given by the Raman spectrum of liquid monodeuterobenzene, are as follows : A_1(C 2) = 1591·1 cm.$^{-1}$ and B_1(C 2) = 1574 cm.$^{-1}$. One observes that the frequency separation between the two vibrations is slightly greater in the upper electronic state than in the ground state, just as with 1 : 4-dideuterobenzene.

(4) *Band Series* G, G′, H, H′, h′, I, I′, i′, i″, J, *and* j.—These bands are concerned in various ways with the already mentioned out-of-plane vibrations A_2(C) and B_2(C). Series G and G′ resemble the correspondingly named series in the absorption spectrum of 1 : 4-dideuterobenzene (Part VIII, Section 4). Characteristically, their band-series involve a gain of two quanta of the vibrations B_2(C) and A_2(C), respectively, in combination in either case with the electronic and vibrational transitions of series A. Similarly, the bands of series H and H′ involve gains of two quanta of the vibrations B_2(C) and A_2(C), respectively, in association with the electronic and vibrational transitions of series B. Series h′, which is represented in the spectrum by a single band only, corresponds to series H′, except for the additional presence in each of the combining states of one quantum of either vibration A_1(C 1) or vibration B_1(C 1). Bands corresponding to I_0 and I_0' were not found in the spectrum of 1 : 4-dideuterobenzene, but these bands have an identified analogue in the band I_0^0 of the absorption spectrum of benzene : band I_0 is considered to involve the gain of two quanta of the vibration B_2(C), whilst band I_0' is regarded as arising from the gain of one quantum of each of the vibrations B_2(C) and A_2(C) in a transition from the " vibrationless " ground state. Band i_0' is associated with a loss of two such quanta in a transition from the binary combination level of the B_2(C) and A_2(C) vibrations of the electronic ground state to the " vibrationless " level of the electronically excited state. Finally, band i_0'' is connected with a similar loss of two quanta of the vibration A_2(C) in a transition from the first overtone level of this vibration in the ground state to the " vibrationless " level of the excited state.

Series J is concerned with transitions characterised by the excitation of either or both of the vibrations A_2(C) and B_2(C) under the condition that the total number of their quanta in the lower state is the same as the total number in the upper state. In this series the spectral activity is entirely due to these sequence-forming vibrations, and we connect with this the circumstance that the strong preference, shown in the sequences of most other series for totally symmetrical combinations of these vibrations, does not here arise (cf. Part VIII, Section 4). Accordingly, the main sequence of the J series, like those of the J series of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene, exhibits what we call " complex branching " : it includes many bands in which each individual vibration is present with different quantum numbers in the two combining states. The main sequence therefore appears here, just as in the absorption spectra of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene, as an array of numerous weak bands, which, except for a few gaps, fill the spectrum for a region extending over several hundred wave-numbers on the long-wave side of the electronic origin. Part of the sequence is repeated in the present spectrum with a positive displacement by the usual progression interval. Series j is similar to series J except that each of the combining states now possesses additionally

one quantum of either the vibration A_1(C 1) or the vibration B_1(C 1). This series is less fully developed than the other, but it also shows " complex branching ", like the similar series of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene (Part VIII, Section 4, and Part IX, Section 4).

The series discussed in this Section, together with the already considered sequences of series A—D, furnish the following fundamental vibration frequencies :

$A_2(C)_{ground} = 404$ cm.$^{-1}$ $\quad A_2(C)_{excited} = 243$ cm.$^{-1}$
$B_2(C)_{ground} = 380$ cm.$^{-1}$ $\quad B_2(C)_{excited} = 230$ cm.$^{-1}$

The two A_2(C) frequencies agree with the E_u^+(C) frequencies of benzene and with the A_u(C) frequencies of 1 : 4-dideuterobenzene : as we have remarked before, these vibrations are identical in the three benzenes. The two ground-state frequencies agree with previous values : Herzfeld, Ingold, and Poole gave the value 405 cm.$^{-1}$, largely on the evidence provided by Raman and infra-red combination tones (*J.*, 1946, 316); whilst Bailey *et al.* measured the infra-red fundamental band B_2(C) and gave 380 cm.$^{-1}$ as the frequency of the Q branch (*loc. cit.*).

(5) *Band Series* K, k, K′, *and* L.—We concur with Beck and Sponer in the view that the bands of the series here called K and L, which are found negatively displaced by 134 cm.$^{-1}$ from the bands of series A and B, respectively, are to be correlated, as nearly as the different symmetries of the molecules allow, with the bands of the series, also called K and L, which appear prominently in the absorption and fluorescence spectra of hexadeuterobenzene (Part IV, Section 5, and Part V, Section 4). These series were connected with 1—1 transitions of the hexagonal, out-of-plane vibration A_{2u}(H). The K and L bands in the present spectrum are thus regarded as arising in 1—1 transitions of the vibration B_2(H 1), in combination with the electronic and vibrational transitions of series A or B. The bands of series k are similarly related to series C, and a corresponding explanation is applied to them. The vibration B_2(H 1) is that which in the ground state furnishes the very strong band of lowest frequency in the infra-red spectrum; and from the known frequency of this band, and the difference-frequency, 134 cm.$^{-1}$, we can compute the fundamental frequency in the upper electronic state. Consistently, we find a band, K_0', 951 cm.$^{-1}$ above A_0^{0-0}, which evidently represents the excitation in the upper state of the first overtone of this vibration, in combination with the transitions of the main active origin. From the position of this band, and from the difference frequency, we derive the following fundamental frequencies :

$B_2(H\ 1)_{ground} = 610$ cm.$^{-1}$ $\quad B_2(H\ 1)_{excited} = 476$ cm.$^{-1}$

The ground-state frequency as evaluated in the infra-red spectrum, is 608 cm.$^{-1}$ (Bailey *et al.*, *loc. cit.*).

(6) *Band Series* M, M′, N, N′, O, O′, *and* P.—Series M, N, O, and P correspond exactly to the similarly named series in the absorption spectrum of benzene (Part II, Section 6), and likewise to those which appear in the spectrum of 1 : 4-dideuterobenzene (Part VIII, Section 6). In all these spectra, series M and N consist of bands negatively displaced by 265 cm.$^{-1}$ below the bands of series A and B, respectively; whilst series O and P consist of bands positively displaced by 1170 cm.$^{-1}$ above the bands of series A and B. The vibration concerned is identical in the three benzenes, because the atoms on that para-axis, which in the deuterated compounds contains the deuterium atoms, do not move. It is the E_g^-(H) vibration of benzene, the B_{2g}(H) vibration of 1 : 4-dideuterobenzene, and the A_2(H′) vibration of monodeuterobenzene; and, in each case, it consists of counter-rotatory motions of the carbon and hydrogen hexagons about the common para-axis. Series M and N arise from 1—1 transitions of this vibration, in combination with the transitions of series A and B, respectively, whilst series O and P are produced by upward 0—2 transitions of the same vibration in a similar state of combination with A or B transitions.

Series M′, N′, and O′ are in our assignments constituted similarly to series M, N, and O, respectively, except that the characteristic vibration now corresponds, as nearly as the different symmetries of the molecules allow, to the second component of the degenerate vibration, E_g^-(H), of benzene. This vibration of monodeuterobenzene is called B_2(H′ 1), and its form and frequency have become considerably modified by the presence of the deuterium atom. The difference between its fundamental frequencies in the lower and the upper states is now reduced to 226 cm.$^{-1}$, and it is by this interval that the bands of series M′ and N′ are displaced below the bands of series A and B. Similarly the positive displacement in series O′ is reduced to 1103 cm.$^{-1}$.

These data allow us to compute the following fundamental frequencies :

$A_2(H')_{ground} = 850$ cm.$^{-1}$ $\quad A_2(H')_{excited} = 585$ cm.$^{-1}$
$B_2(H'\ 1)_{ground} = 778$ cm.$^{-1}$ $\quad B_2(H'\ 1)_{excited} = 552$ cm.$^{-1}$

The ground-state values, as given in the Raman spectrum of liquid monodeuterobenzene, are $A_2(H') = 849{\cdot}9$ cm.$^{-1}$, and $B_2(H'\ 1) = 778{\cdot}7$ cm.$^{-1}$ (Bailey *et al.*, *loc. cit.*).

(7) *Band Series* Q, R, S, *and* T.—We deal in this section with the band series which arise from excitations of the three remaining vibrations of B_2 symmetry class. Series Q and R consist of bands negatively displaced by 338 cm.$^{-1}$ below the bands of series A and B, respectively. In explanation of these bands, we assume 1—1 transitions of the relevant vibration in combination with the electronic and vibrational transitions of series A and B. The interval 338 cm.$^{-1}$ thus represents the difference between the fundamental frequencies of the vibration in the two electronic states, and the magnitude of the difference suggests that the vibration concerned is that which is most nearly analogous to the trigonal out-of-plane vibration, B_{2g}(C), of benzene (cf. Parts II and IV). This vibration of monodeuterobenzene is labelled $B_2(C')$. Its fundamental frequency in the lower electronic state is known from infra-red measurements to be 698 cm.$^{-1}$ (Bailey *et al.*, *loc. cit.*), and we have to use this value for the computation of the upper-state fundamental frequency, since we have been unable to identify its overtone in the recorded ultraviolet spectrum. On the other hand, we recognise two other upper-state overtones in the constitution of band series S and T, which are assigned as involving upward 0—2 transitions of the vibrations $B_2(H\ 2)$ and $B_2(H'\ 2)$, respectively, in combination with the electronic and vibrational transitions of series A. These assignments, which are well borne out by comparisons among the different isotopic benzenes (Part XI), provide the following fundamental frequencies:

$$B_2(C')_{excited} = 360 \text{ cm.}^{-1} \qquad B_2(H\ 2)_{excited} = 690 \text{ cm.}^{-1}$$
$$B_2(H'\ 2)_{excited} = 720 \text{ cm.}^{-1}$$

The corresponding fundamental frequencies of the electronic ground state, as given in the infra-red spectrum, are $B_2(C') = 698$ cm.$^{-1}$, $B_2(H\ 2) = 922$ cm.$^{-1}$, and $B_2(H'\ 2) = 995$ cm.$^{-1}$.

(8) *Band Series* X′, x′, X″, Y, *and* Y‴.—These series are characterised by excitations in the upper electronic state of one or another of the various hydrogen-stretching vibrations. We can distinguish band series connected with the single deuterium-stretching vibration and with three of the five protium-stretching vibrations. The band Y_0^{0-0}, which lies 2348 cm.$^{-1}$ above A_0^{0-0}, is attributed to the excitation of one quantum of the deuterium-stretching vibration, in combination with the electronic and vibrational transitions of A_0^{0-0}. The band has no other probable explanation, and the frequency separation is the same, to within a few wave numbers, as that of the corresponding band in the absorption spectrum of 1 : 4-dideuterobenzene (Part VIII, Section 8). We should expect to find a band of appreciable intensity 2348 cm.$^{-1}$ above the electronic origin, but the presence of such a band cannot be verified, because this position coincides with that of the strong band A_2^{0-0}.

The series X′ starts with a band of moderate intensity, 3072 cm.$^{-1}$ above the electronic origin. We here assume a transition from the "vibrationless" ground state to the fundamental level of one of the protium-stretching vibrations in the upper electronic state. The band starts a progression of two members and also a sequence of two members. The bands of the weak series x′ are displaced below those of series X′ by 86 cm.$^{-1}$, so that series x′ is related to series X′ just as C is to A or as D is to B. For series x′ we assume the additional presence, in each of the combining states, of one quantum of one of the main perturbing vibrations, A_1(C 1) or B_1(C 1). We tentatively ascribe the band $X_0''^{0-0}$, situated 3081 cm.$^{-1}$ above the electronic origin, to a transition from the "vibrationless" ground state to the one-quantum level in the upper electronic state of another of the protium-stretching vibrations. Finally, we interpret the band $Y_0'''^{0-0}$, lying 3129 cm.$^{-1}$ above A_0^{0-0}, as arising in a transition which combines an excitation in the upper electronic state of one quantum of a third of the protium-stretching vibrations with the electronic and vibrational changes associated with A_0^{0-0}.

As to the assignment of the three protium-stretching frequencies of the upper state, 3072, 3081, and 3129 cm.$^{-1}$, among the five relevant normal modes of vibration, we can immediately identify the frequency 3072 cm.$^{-1}$ as belonging to the vibration $B_1(H\ 2)$, on account of the intensity with which it appears with a direct displacement from the electronic origin. This strongly suggests that the vibration is a close analogue of the $E_g^+(H\ 1)$ vibration of benzene, and of the $B_{1g}(H\ 2)$ vibration of 1 : 4-dideuterobenzene. The frequencies are consistent with this assignment. The normal co-ordinate of the vibration $B_1(H\ 2)$ of monodeuterobenzene (cf. *J.*, 1946, 306, diagram V) is very nearly identical with that of the $B_{1g}(H\ 2)$ vibration of 1 : 4-dideuterobenzene, and with one of the normal co-ordinates of the degenerate vibration, $E_g^+(H\ 1)$, of benzene. The equivalence is not exact because of the coupling of the protium motions, but this is always very weak. We therefore expect the frequencies to be the same to

within a few wave numbers. The value given for the upper-state frequency for the benzene vibration was 3080 cm.$^{-1}$ (cf. Part II), and for the 1 : 4-dideuterobenzene vibration was 3075 cm.$^{-1}$ (cf. Part VIII), so that our present value, 3072 cm.$^{-1}$, for the monodeuterobenzene frequency is about what we should expect.

Another of the protium-stretching frequencies which we can identify with fair certainty is 3129 cm.$^{-1}$. This is recorded in the spectrum as a displacement from the main active origin A_0^{0-0}, and not from the electronic origin. It therefore presumably belongs to that vibration which most closely approximates to the totally symmetrical protium-stretching vibration, A_{1g}(H), of benzene, or to the totally symmetrical protium-stretching vibration, A_g(H 2) of 1 : 4-dideuterobenzene. In monodeuterobenzene this vibration will be the one in which all five protium bonds stretch and contract in phase (cf. *J.*, 1946, 306, diagram II). The benzene frequency was 3130 cm.$^{-1}$, and the 1 : 4-dideuterobenzene frequency was 3132 cm.$^{-1}$ (Parts II and VIII), and therefore the value, 3129 cm.$^{-1}$, found for the most nearly analogous vibration, A_1(H 2), of monodeuterobenzene seems reasonable.

The third upper-state protium-stretching frequency, 3081 cm.$^{-1}$, is assigned to the vibration A_1(H′ 2), on the negative ground that the remaining two protium-stretching vibrations would hardly be expected to appear in the spectrum. This follows from a consideration of their normal co-ordinates. Approximate diagrams of these have been given by Bailey *et al.* (*J.*, 1946, 306, diagrams IV and VI), and, to this approximation, both vibrations are antisymmetric with respect to the centre of symmetry of the electronic system. The selection rules show that the fundamental frequency of an exactly *ungerade* vibration could not be excited in a transition, like the present one, from a *gerade* to an *ungerade* electronic state (Part I, Section 4, *et seq.*). It is no doubt for a similar reason that the same vibrations in the ground state, although theoretically allowed in the Raman spectrum inasmuch as they are not exactly *ungerade*, cannot in fact be observed in that spectrum. The actual vibration to which we assign the upper-state frequency 3081 cm.$^{-1}$ is not even approximately *ungerade* (*cf. loc. cit.*, diagram III). Its upper-state fundamental frequency should therefore be excited with appreciable intensity in the ultraviolet absorption spectrum, just as its lower-state fundamental frequency should appear in the Raman spectrum, where in fact it has been recognised.

The following upper-state fundamental frequencies result from these assignments :

$A_1(\text{H } 1)_{\text{excited}} = 2348$ cm.$^{-1}$ $\quad A_1(\text{H } 2)_{\text{excited}} = 3129$ cm.$^{-1}$
$A_1(\text{H}' 2)_{\text{excited}} = 3081$ cm.$^{-1}$ $\quad B_1(\text{H } 2)_{\text{excited}} = 3072$ cm.$^{-1}$

Corresponding fundamental frequencies of the lower electronic state, as obtained from the Raman spectrum of liquid monodeuterobenzene, are as follows : A_1(H 1) = 2269·0 cm.$^{-1}$, A_1(H 2) = 3054·0 cm.$^{-1}$, A_1(H′ 2) = 3060 cm.$^{-1}$, B_1(H 2) = 3041 cm.$^{-1}$ (Bailey *et al.*, *loc. cit.*). As usual, the hydrogen-stretching frequencies of the upper electronic state are all somewhat larger than the corresponding frequencies of the electronic ground state.

(9) *Band Series z and z′.*—These series start with bands displaced by 2443 cm.$^{-1}$ above the active origins A_0^{0-0} and B_0^{0-0}, respectively. The common displacement is presumably the frequency of an overtone or combination tone derived from vibrations whose fundamental frequencies in the upper electronic state are not exactly known. It would be plausible to suppose, for instance, that the frequency 2443 cm.$^{-1}$ represents the upper-state first overtone of one of the five planar protium-bending vibrations, whose frequencies in the electronic ground state range from 1031 cm.$^{-1}$ to 1292 cm.$^{-1}$. In the absence of additional evidence, we are not able to make a more definite suggestion.

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105. *Excited States of Benzene. Part XI. Comparisons between the First Ultraviolet Absorption and Fluorescence Band Systems of Isotopically Isomeric Benzenes, and Further Determinations of the Vibration Frequencies of the Upper Electronic State.*

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Consideration is given to the assignment of observed frequencies to vibrations of the upper electronic state, and also to the indirect determination of a number of upper-state vibration frequencies which have not been spectrally observed. Both subjects are discussed on the basis of

comparisons between the ultraviolet spectra of the different isotopically isomeric benzenes, the central principle being that isotopic substitution cannot change the forces acting in any given electronic state. Two methods are employed, both new in the study of excited polyatomic molecules, though well known in their application to normal molecules. One is the use of the product theorem in order to provide relationships between the upper-state fundamental frequencies of vibrations of the various isotopic isomerides. The other consists in the calculation, from a limited number of upper-state frequencies, of a simplified force-system, applicable in common to all the excited molecules, and the subsequent use of this system for the approximate location of other upper-state frequencies, and thus for their eventual determination by reference back to the spectra. In these ways, assignments of many observed frequencies to upper-state vibrations are made or justified, and some unobserved vibration frequencies of the excited molecules are calculated. The determined fundamental frequencies of the upper electronic states of all the benzenes studied are correlated in tables.

Scope.—In the preceding papers we have been dealing with individual absorption and fluorescence spectra of the various isotopic isomerides of benzene. In those papers we have given a detailed interpretation of each spectrum, but have presented the supporting arguments only in so far as they could be based in each case on the internal evidence of the spectrum under consideration. An important section of the basis of the interpretation depends, however, on comparisons between the different spectra, particularly on comparisons of the absorption and fluorescence spectra of one isotopic form of benzene with those of another. These arguments of comparison we now present, thus completing the foundations of the assignments already given.

In making the comparisons, we shall introduce two methods, neither of which has before been applied to the study of electronic spectra of polyatomic molecules. The first (Section A) is the use of the product theorem of Teller and Redlich, in order to provide calculable relationships between the fundamental frequencies of isotopically isomeric molecules in their electronically excited states. Hitherto it has been implicit in all discussions of the product theorem that electronic ground states are under consideration; and all previous applications have been to ground states. But there is clearly no reason of principle why the theorem should not be applied to any electronically excited state which is sufficiently long-lived to give sharp vibrational energy levels.

The second method (Section B) consists in the calculation, from a limited number of determined frequencies, of a simplified force-system for the electronically excited state (the same system for all isotopically isomeric forms of the molecule), and the subsequent use of the system for the approximate location of other fundamental frequencies, and thus for their eventual identification by reference back to the spectra. Force systems have commonly been thus employed in the study of polyatomic molecules in their electronic ground states, but we know of no previous attempt to set up and use such a force-system for a polyatomic molecule in an excited state. Since, without these methods, our assignments of bands to vibration frequencies, and of frequencies to vibrations, could not have been nearly as extensive as they actually are, it seems that the two working tools whose employment is here introduced have some general importance for the electronic spectroscopy of polyatomic molecules.

(A) *Product Theorem applied to the Excited State.*

(1) *Theoretical Product Ratios for the* $\mathbf{B_{2u}}$ *State.*—The product theorem is, in general principle, a complete statement of the relationships which subsist between the fundamental vibration frequencies of two isotopically isomeric molecules, in an arbitrary but identical electronic state, with an arbitrary but harmonic potential system. The relationships take the form of theoretically given ratios, for pairs of isotopically isomeric molecules, of the products of complete sets of frequencies of vibrations of the same symmetry class, if the molecules have identical symmetry; or of products of the sets of frequencies of vibrations of corresponding sets of symmetry classes, if the molecules have different symmetry. The general formula, together with an explanation of the symbols, as they must be understood when the molecules have like symmetry, and when they have unlike symmetry, has been given in a former paper (*J.*, 1946, 232). In the same paper a number of theoretical product ratios were evaluated for the ground state, $\mathbf{A_{1g}}$, of benzene.

The only point of difference which has to be taken into account in calculating theoretical ratios for the excited state, $\mathbf{B_{2u}}$, of benzene arises from the slightly different dimensions of the excited molecule. We know that both the normal and the excited molecules possess the same symmetry, $\mathbf{D_{6h}}$. However, the excited molecule is somewhat larger than the other, as is shown by the degradation of the rotational structure of bands towards the red in both absorption and fluorescence spectra. From a semi-quantitative estimate of the variation of band intensity along the main totally symmetrical progressions, in particular, from the result that the second members

of such progressions are the strongest members, whilst the first and third possess about equal intensity, it is possible independently to estimate the increase of size accompanying the electronic excitation. Using both methods, Sponer, Nordheim, Sklar, and Teller have estimated that the C–C bond-length increases by 1·2—1·5% (*J. Chem. Physics*, 1939, **7**, 207). From our analysis of the spectra, we shall conclude (Part XII) that the C–C bond-length increases by 2·5%, whilst the C–H bond-length decreases by 1·0%, as a result of the electronic excitation. We take these values in calculating upper-state product ratios.

Some theoretical product ratios for the electronically excited state are given in Table I. They are called harmonic values, because of the neglect of the anharmonicity of the vibrations. Just as for the ground state (*J.*, 1946, 233), so also for the excited state, the general effect of anharmonicity should be to cause the ratios of the products of observed frequencies to fall slightly below the theoretical ratios here given. This is borne out by our experience. The effect of anharmonicity on the observed product ratios of the excited state is very similar in magnitude to the previously found effect on the product ratios of the ground state; and therefore, in calculating frequencies of the excited state from the product ratios, we make an allowance for anharmonicity according to the same scale as that adopted in the former calculations relating to the ground state (*loc. cit.*).

TABLE I.

Theoretical (Harmonic) Values of the Frequency Product Ratios for Some Pairs of the Excited Molecules C_6H_6, C_6H_5D, 1 : 4-$C_6H_4D_2$, 1 : 3 : 5-$C_6H_3D_3$, 1 : 2 : 4 : 5-$C_6H_2D_4$, *and* C_6D_6.

(a) *Greatest common symmetry* D_{6h}.

Symmetry class.	$\frac{C_6H_6}{C_6D_6}$	Symmetry class.	$\frac{C_6H_6}{C_6D_6}$	Symmetry class.	$\frac{C_6H_6}{C_6D_6}$
A_{1g}	1·414	B_{1u}	1·414	E_g^+	1·978
A_{2g}	1·291	B_{2g}	1·414	E_u^+	1·414
A_{2u}	1·362	B_{2u}	1·414	E_g^-	1·291
				E_u^-	1·925

(b) *Greatest common symmetry* D_{3h}.

D_{6h} Classes.	D_{3h} Class.	$\frac{C_6H_6}{C_6H_3D_3}$	$\frac{C_6H_3D_3}{C_6D_6}$	D_{6h} Classes.	D_{3h} Class.	$\frac{C_6H_6}{C_6H_3D_3}$	$\frac{C_6H_3D_3}{C_6D_6}$
A_{1g}, B_{1u}	A_1'	1·414	1·414	E_g^+, E_u^-	E'	1·960	1·962
A_{2g}, B_{2u}	A_2'	1·346	1·352	E_u^+, E_g^-	E''	1·346	1·352
A_{2u}, B_{2g}	A_2''	1·387	1·388				

(c) *Greatest common symmetry* V_h.

D_{6h} Classes.	V_h class.	$\frac{C_6H_6}{C_6H_4D_2}$	$\frac{C_6H_6}{C_6H_2D_4}$	$\frac{C_6H_4D_2}{C_6H_2D_4}$	$\frac{C_6H_4D_2}{C_6D_6}$	$\frac{C_6H_2D_4}{C_6D_6}$
A_{1g}, E_g^+	A_g	1·414	1·998	1·414	1·998	1·414
A_{1u}, E_u^+	A_u	1·000	1·414	1·414	1·414	1·000
A_{2g} E_g^+	B_{1g}	1·368	1·877	1·371	1·884	1·373
A_{2u}, E_u^+	B_{1u}	1·396	1·380	0·988	1·380	1·396
B_{1g}, E_g^-	B_{2g}	1·000	1·291	1·291	1·291	1·000
B_{1u}, E_u^-	B_{2u}	1·396	1·948	1·396	1·948	1·396
B_{2g}, E_g^-	B_{3g}	1·326	1·369	1·031	1·374	1·331
B_{2u}, E_u^-	B_{3u}	1·396	1·948	1·396	1·948	1·396

(d) *Greatest common symmetry* C_{2v}.

D_{6h} classes.	C_{2v} class.	$\frac{C_6H_6}{C_6H_5D}$	$\frac{C_6H_5D}{C_6H_4D_2}$	$\frac{C_6H_5D}{C_6H_3D_3}$	$\frac{C_6H_5D}{C_6H_2D_4}$	$\frac{C_6H_5D}{C_6D_6}$
A_{1g}, B_{1u}, E_g^+, E_u^-	A_1	1·405	1·405	1·973	2·773	5·474
A_{2g}, B_{2u}, E_g^+, E_u^-	B_1	1·382	1·383	1·910	2·649	5·072
A_{1u}, B_{1g}, E_u^+, E_g^-	A_2	1·000	1·000	1·346	1·821	1·823
A_{2u}, B_{2g}, E_u^+, E_g^-	B_2	1·359	1·362	1·375	1·387	2·583

(2) *Excited* C_6H_6 *and* C_6D_6: *The* A_{1g} *Vibrations* (cf. Part II, Sections 2 and 7; and Part IV, Sections 2 and 7).—The fundamental frequencies of the ring-swelling vibration, A_{1g}(C), are well established: they are 923 cm.$^{-1}$ for excited benzene and 879 cm.$^{-1}$ for excited hexadeuterobenzene. The fundamental frequency of the hexagonal hydrogen-stretching vibration, A_{1g}(H), of benzene,

3130 cm.$^{-1}$, also appears clearly from the analysis of the absorption spectrum of benzene (Part II, Section 7).

On the other hand, the frequency of the totally symmetrical hydrogen-stretching vibration of hexadeuterobenzene does not unambiguously emerge from our analysis of the absorption spectrum of that substance. We have suggested that the relevant band is that at 40146 cm.$^{-1}$, in which case the vibration frequency would be 2357 cm.$^{-1}$ (*Nature*, 1946, **158**, 163). But the band has another conceivable explanation (Part IV, Table I), and there may be overlapping bands in this region. Therefore we have calculated this fundamental frequency, from those mentioned in the preceding paragraph, with the help of the product rule. We find:

$$\text{For } C_6D_6 :— A_{1g}(H)_{\text{excited}} = 2340 \text{ cm.}^{-1}$$

Just as for benzene, this frequency of excited hexadeuterobenzene is a little above the corresponding frequency for the normal state of that substance, 2292·6 cm.$^{-1}$, as given by the Raman spectrum of liquid hexadeuterobenzene (Poole, *J.*, 1946, 245), or 2286 cm.$^{-1}$, as given by the fluorescence spectrum of hexadeuterobenzene vapour (Part IV, Section 6).

(3) *Excited* C_6H_6 *and* C_6D_6: *The* B_{1u} *Vibrations.*—These vibrations do not appear to leave any record of their frequencies in the ultraviolet spectra of benzene and hexadeuterobenzene. On the other hand, the two A_{1g} and two B_{1u} vibrations of each of these compounds are collectively related through the product theorem to the four A_1' vibrations of 1 : 3 : 5-trideuterobenzene, and we know the frequencies of all four of these vibrations of excited 1 : 3 : 5-trideuterobenzene from our analysis of the appropriate absorption spectrum (Part VI, Sections 2 and 8). It is therefore possible to calculate the product of the two B_{1u} frequencies for excited benzene, and for excited hexadeuterobenzene.

On account of the weak coupling of hydrogen-stretching vibrations, the frequency of the trigonal hydrogen-stretching vibration, $B_{1u}(H)$, either for excited benzene or for excited hexadeuterobenzene, must be very nearly identical with that of the corresponding hexagonal hydrogen-stretching vibration, $A_{1g}(H)$. By assuming exact equivalence, we can use the calculated frequency products to compute, with very little error, the frequencies of the trigonal carbon-bending vibrations, $B_{1u}(C)$, of excited benzene and hexadeuterobenzene. We thus obtain the following data:

$$\text{For } C_6H_6 :— B_{1u}(C)_{\text{excited}} = 985 \text{ cm.}^{-1}; \quad B_{1u}(H)_{\text{excited}} = 3130 \text{ cm.}^{-1}$$
$$\text{For } C_6D_6 :— B_{1u}(C)_{\text{excited}} = 940 \text{ cm.}^{-1}; \quad B_{1u}(H)_{\text{excited}} = 2340 \text{ cm.}^{-1}$$

The corresponding fundamental frequencies for the ground state of benzene are $B_{1u}(C) = 1010$ cm.$^{-1}$ and $B_{1u}(H) = 3060$ cm.$^{-1}$, and for the ground state of hexadeuterobenzene, $B_{1u}(C) = 963$ cm.$^{-1}$ and $B_{1u}(H) = 2290$ cm.$^{-1}$. These figures, given by Herzfeld, Ingold, and Poole, are based largely on Raman and infra-red combination tones (*J.*, 1946, 316). Thus the carbon-bending frequencies are a little reduced, and the hydrogen-stretching frequencies are a little raised, by the electronic excitation.

It is useful to check the four frequencies of the excited state against the product theorem, since the B_{1u} product ratio is not determined by the ratios employed in the calculation of the frequency products. We find:

$$\frac{\Pi B_{1u}(C_6H_6^*)}{\Pi B_{1u}(C_6D_6^*)} = \frac{985 \times 3130}{940 \times 2340} = 1{\cdot}403 \text{ (Harmonic value } 1{\cdot}414) \dagger$$

(4) *Excited States of* C_6H_6 *and* C_6D_6. *The* E_g^+ *Vibrations* (cf. Part II, Sections 2, 3, and 7; and Part IV, Sections 2, 3, 7, and 11).—Three of the four fundamental frequencies of this symmetry class are definitely known for both excited benzene and excited hexadeuterobenzene. The carbon-bending vibrations of benzene and hexadeuterobenzene have the frequencies 521 cm.$^{-1}$ and 499 cm.$^{-1}$, the carbon-stretching vibrations the frequencies 1470 cm.$^{-1}$ and 1403 cm.$^{-1}$, and the hydrogen-stretching vibrations the frequencies 3080 cm.$^{-1}$ and 2320 cm.$^{-1}$, respectively. The difficulty has been with the hydrogen-bending vibration. The absorption spectrum of benzene gives no clear indication of the frequency of this vibration in the upper electronic state. The absorption spectrum of hexadeuterobenzene indicates, but does not firmly establish, the value 830 cm.$^{-1}$. However, indirect support for a value in this close neighbourhood is obtained in the absorption spectrum of 1 : 3 : 5-trideuterobenzene (Part VI, Section 3); and we have two independent theoretical reasons for expecting a value only slightly lower than the

† In this and similar formulæ the excited (B_{2u}) state is distinguished by an asterisk.

ground-state value 867 cm.$^{-1}$ (Part XII). Therefore we adopt the value 830 cm.$^{-1}$ as probably correct, and calculate the corresponding benzene frequency with the aid of the product rule :

$$\text{For } C_6H_6 :—E_g^+(\text{H } 2)_{\text{excited}} = 1130 \text{ cm.}^{-1}$$

A band of moderate or low intensity displaced by this amount above the electronic origin would be difficult to distinguish in the absorption spectrum of benzene, because it would fall (Part II, Table I) amongst the peaks of a rather strong and complex band (Part II, Sections 2 and 4) of the main series (band A_1^2). The calculated frequency may be somewhat inexact, because the product ratio contains the above-mentioned carbon-stretching frequencies, and these themselves, as we have remarked in the papers cited, may have been rendered inexact by resonance displacement of the relevant bands. The hydrogen-bending frequency for the ground state of benzene is 1178 cm.$^{-1}$ (cf. *J.*, 1946, 332).

(5) *Excited States of* C_6H_6 *and* C_6D_6. *The* E_g^- *Vibration* (cf. Part II, Section 5; Part III, Section 4; Part IV, Section 6; and Part V, Section 5).—Amongst the most prominent of the sequence frequencies appearing in the absorption and fluorescence spectra of benzene and hexadeuterobenzene are those which have the values 265 cm.$^{-1}$ for benzene and 208 cm.$^{-1}$ for hexadeuterobenzene. They obviously correspond to each other, and represent differences between the lower- and the upper-state fundamental frequencies of the same vibration. The intensities with which the bands appear suggest Boltzmann factors belonging to frequencies around the region 500—800 cm.$^{-1}$, thus excluding assignment to any but out-of-plane vibrations. Even two of these, the vibrations E_u^+(H) and B_{2g}(H), are probably to be excluded on grounds of intensity, and a third, E_u^+(C), having known frequencies, is already excluded; so that we are left with the following possibilities, *viz.*, E_g^-(H), A_{2u}(H), and B_{2g}(C). The spectra themselves provide reason for the belief that the vibration concerned in these difference frequencies is degenerate, and thus the vibration E_g^-(H) is indicated.

Now any trial assignment can be checked by subtracting the observed difference frequencies from the known ground-state frequencies corresponding to the assignment, and applying the product rule to the upper-state frequencies thus computed. This use of the product theorem supports the choice of E_g^-(H), excludes A_{2u}(H), and has nothng immediately to say about B_{2g}(C). However, the B_{2g}(C) assignment can be excluded by a force-field calculation (Section B, 2); and a later application of the product rule assigns to the upper-state frequencies of this vibration, as well as of the vibration B_{2g}(H), values quite other than those they would have to possess if made responsible for the difference frequencies under discussion. The product theorem does not of itself exclude assignment of the difference frequencies to the vibration E_u^-(H); but if, in spite of the contrary indication of the intensities, we should try so to assign the differences, a force-field calculation would lead us back to almost the same E_g^-(H) frequencies as those which follow from our preferred assignment (Section B, 2).

This assignment leads to the E_g^-(H) frequencies 585 cm.$^{-1}$ for the upper state of benzene, and 454 cm.$^{-1}$ for that of hexadeuterobenzene. A final argument in favour of the assignment is that, just as in the fluorescence spectra of benzene and hexadeuterobenzene we observe prominent intervals representing the first overtones of the known ground-state frequencies of the E_g^-(H) vibration, so in the absorption spectra we find a corresponding appearance of intervals which, if interpreted as overtones, agree in both cases with the computed upper-state frequencies of this vibration.

The product ratio for the E_g^- symmetry class in the upper electronic states of benzene and hexadeuterobenzene is as follows :

$$\frac{\Pi E_g^-(C_6H_6^*)}{\Pi E_g^-(C_6D_6^*)} = \frac{585}{454} = 1{\cdot}288 \text{ (Harmonic value} = 1{\cdot}291)$$

A similarly close agreement between the observed and the calculated ratios for this symmetry class was found for the electronic ground state (Poole, *J.*, 1946, 252).

(6) *Excited States of* C_6H_6 *and* C_6D_6. *The* E_u^+ *Vibrations.*—The fundamental frequencies of the vibration E_u^+(C) in the lower and the upper states of benzene and hexadeutetobenzene are well established by the fluorescence and absorption spectra of these compounds (Part II, Section 4; Part III, Section 3; Part IV, Section 3; and Part V, Section 3). The difference frequencies 161 and 141 cm.$^{-1}$ have been proved to belong to this vibration (cf. Part I, Section 4), and its observed overtones of the ground state agree with the independently known fundamental frequencies in the ground state; furthermore, its observed overtones of the excited state agree with upper-state fundamental frequencies, as computed from the ground-state fundamentals and the difference frequencies.

Another out-of-plane vibration of which the upper-state frequencies may be regarded as well established is the vibration, E_g^-(H), discussed in the preceding sub-section. Therefore the next step in the assignment of upper-state frequencies to the out-of-plane vibrations is to base on the determined frequencies of these two vibrations a force-field calculation. In this way we may compute frequencies, in the upper state of benzene and hexadeuterobenzene, of the vibration E_u^+(H). Then having thus roughly located these frequencies (Section B, 2), we refer back to the absorption spectra of benzene and hexadeuterobenzene, in which the frequencies can now be recognised as overtones and in certain combinations, and thus more exactly determined (Part II, Section 8; Part IV, Section 10). Confirmation follows from the verified prediction that the benzene frequency should also belong to the upper state of the 1 : 4-dideuterobenzene, and thus reappear in the absorption spectrum of that substance; whilst the hexadeuterobenzene frequency should for similar reasons be found again in the absorption spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene (Part VIII, Section 5; Part IX, Section 5). Further confirmation follows from an application of the product rule to the E_u^+ vibrations of the upper states of benzene and hexadeuterobenzene:

$$\frac{\Pi E_u^+(C_6H_6^*)}{\Pi E_u^+(C_6D_6^*)} = \frac{243 \times 706}{208 \times 590} = 1{\cdot}398 \text{ (Harmonic value} = 1{\cdot}414)$$

The ground-state frequencies gave the ratio 1·408 (harmonic value, 1·414) (Herzfeld, Ingold, and Poole, *J.*, 1946, 321).

(7) *Excited States of* C_6H_6 *and* C_6D_6. *The* A_{2u} *Vibration* (cf. Part II, Section 5; Part IV, Section 5; and Part V, Section 4).—The absorption and fluorescence spectra of hexadeuterobenzene contain the prominent sequence interval 114 cm.$^{-1}$. Its strength suggests low frequencies, probably belonging to an out-of-plane vibration. But no corresponding interval could be found in either the absorption or the fluorescence spectrum of benzene. The smaller Boltzmann factors associated with the lighter molecule seem an insufficient explanation of this. It appears much more probable that the vibration is a nearly pure hydrogen vibration, and that, in consequence, the sequence interval in benzene is considerably larger than in hexadeuterobenzene, and is, in fact, about 160 cm.$^{-1}$, with the effect that the resulting bands cannot be seen in the presence of the strong bands of the E_u^+(C) sequences.

This hypothesis suggests a trial assignment to the vibration A_{2u}(H). For the only other out-of-plane hydrogen vibration not excluded by previous assignments is the B_{2g}(H) vibration, and it would be difficult to reconcile this either with the observed intensities, or with the presumed difference between the sequence frequencies.† Computing upper-state A_{2u}(H) frequencies from the known lower-state fundamental frequencies and the differences, we obtain values which for both compounds are confirmed by the recognition of first overtones in the relevant spectra. The computed frequencies are consistent with force-field calculations based on the already discussed assignments to the upper electronic state (Section B, 2). An application of the product theorem to the A_{2u} symmetry class of the excited state supplies further confirmation:

$$\frac{\Pi A_{2u}(C_6H_6^*)}{\Pi A_{2u}(C_6D_6^*)} = \frac{513}{382} = 1{\cdot}343 \text{ (Harmonic value} = 1{\cdot}362)$$

In the ground state the observed ratio was 1·351, the harmonic value being 1·362 (Bailey, Carson, and Ingold, *J.*, 1946, 255).

(8) *Excited States of* C_6H_6 *and* C_6D_6. *The* B_{2g} *Vibrations* (cf. Part II, Sections 5 and 8; Part IV, Sections 8 and 9; and Part V, Sections 7 and 8).—The known low values, in excited benzene and hexadeuterobenzene, of the frequencies of the vibration E_u^+(C) lead us to expect upper-state frequencies between 300 and 400 cm.$^{-1}$ for the other out-of-plane carbon vibration B_{2g}(C). Force-field calculations confirm this, and locate the frequencies somewhat more closely (Section B, 2). In the absorption spectrum of benzene, we find a frequency for which the only obvious assignment is that of a first overtone, in the upper electronic state, of a fundamental frequency 365 cm.$^{-1}$. In both the absorption and the fluorescence spectrum of hexadeuterobenzene, we find similar evidence of a fundamental frequency, 306 cm.$^{-1}$, of the upper electronic state. And in confirmation, we are able to distinguish in the latter two spectra a sequence interval 295 cm.$^{-1}$, a frequency which, when added to the upper-state fundamental frequency 306 cm.$^{-1}$, gives correctly the known lower-state fundamental frequency, 601 cm.$^{-1}$, of the B_{2g}(C) vibration of hexadeuterobenzene (Herzfeld, Ingold, and Poole give 601 cm.$^{-1}$, *J.*, 1946, 332).

† The B_{2g}(H) vibration is *not* a nearly pure hydrogen vibration (cf. Bailey, Hale, Herzfeld, Ingold, Leckie, and Poole, *J.*, 1946, 261).

Force-field calculations, based on the previously assigned frequencies of out-of-plane vibrations of the excited electronic states of benzene and hexadeuterobenzene, have been used (Section B, 2) in order to locate approximately the frequencies, in these excited molecules, of the remaining out-of-plane vibration, B_{2g}(H). On referring back to the absorption spectrum of benzene, we find an overtone frequency belonging to an upper-state fundamental frequency 775 cm.$^{-1}$, in good agreement with the calculated B_{2g}(H) frequency for excited benzene. In both the absorption and the fluorescence spectrum of hexadeuterobenzene, we find similar evidence of an upper-state fundamental frequency 663 cm.$^{-1}$, also in good agreement with the calculated B_{2g}(H) frequency for excited hexadeuterobenzene. And in these two spectra we can find a sequence interval 165 cm.$^{-1}$, a frequency which, when added to the upper-state fundamental frequency 663 cm.$^{-1}$, gives correctly the known fundamental frequency, 828 cm.$^{-1}$, of the B_{2g}(H) vibration in the ground state of hexadeuterobenzene (Herzfeld, Ingold, and Poole give 827 cm.$^{-1}$, *loc. cit.*).

On the evidence presented, each of these pairs of assignments would seem fairly secure, but we can apply an additional check to the whole set by the use of the product theorem. We thus find :

$$\frac{\Pi B_{2g}(C_6H_6^*)}{\Pi B_{2g}(C_6D_6^*)} = \frac{365 \times 775}{306 \times 663} = 1{\cdot}394 \text{ (Harmonic value} = 1{\cdot}414)$$

In the electronic ground state the corresponding ratio was 1·393, the harmonic value again being 1·414 (Herzfeld, Ingold, and Poole, *loc. cit.*).

(9) *Excited State of* 1 : 3 : 5-$C_6H_3D_3$. *The E″ Vibrations* (cf. Part VI, Sections 2, 4, 5, and 6; Part VII, Sections 3 and 4).—This symmetry class contains one carbon and two hydrogen vibrations. The first-named, E''(C), corresponds very closely to the benzene and hexadeuterobenzene vibration E_u^+(C). Like the latter it is responsible for the strongest sequences in the absorption and fluorescence spectra, besides appearing as its upper- and lower-state overtones, and identifying itself as a degenerate vibration by the positions of some of the bands. The upper-state fundamental frequency, 223 cm.$^{-1}$, is well established, and its assignment cannot be doubted.

The vibration E''(H 1) roughly corresponds to the vibration E_g^-(H) of benzene and hexadeuterobenzene. Like the latter it appears as a rather strong sequence frequency in the absorption and fluorescence spectra of 1 : 3 : 5-trideuterobenzene, and also as an upper-state overtone in the absorption spectrum, besides confessing itself to be a degenerate vibration by the positions of some of the series. The upper-state fundamental frequency, 495 cm.$^{-1}$, is of the expected magnitude, and the evidence of analogy is so strong that the correctness of its assignment seems certain.

The third vibration, E''(H 2), is the approximate analogue of the benzene and hexadeuterobenzene vibration B_{2g}(H). In the absorption spectrum of 1 : 3 : 5-trideuterobenzene we find an overtone and a difference frequency, which point to an upper-state fundamental frequency 680 cm.$^{-1}$. It is of the expected magnitude for the vibration E''(H 2), and its participation in the difference frequency points to its belonging to a vibration of the E'' class. For confirmation we apply the product theorem :

$$\frac{\Pi E_u^+ E_g^-(C_6H_6^*)}{\Pi E''(C_6H_3D_3^*)} = \frac{243 \times 585 \times 706}{223 \times 495 \times 680} = 1{\cdot}337 \text{ (Harmonic value} = 1{\cdot}346)$$

$$\frac{\Pi E''(C_6H_3D_3^*)}{\Pi E_u^+ E_g^-(C_6D_6^*)} = \frac{223 \times 495 \times 680}{208 \times 454 \times 590} = 1{\cdot}347 \text{ (Harmonic value} = 1{\cdot}352)$$

The results evidently confirm the assignments.

(10) *Excited State of* 1 : 3 : 5-$C_6H_3D_3$. *The A_2'' Vibrations* (cf. Part VI, Section 7; and Part VII, Section 5).—This symmetry class also contains one carbon and two hydrogen vibrations. The carbon vibration, A_2''(C), is a close analogue of the benzene and hexadeuterobenzene vibration, B_{2g}(C). In the absorption spectrum of 1 : 3 : 5-trideuterobenzene we find a frequency which can scarcely be assigned otherwise than as the first overtone of an upper-state fundamental frequency 360 cm.$^{-1}$. Such a frequency could only belong to the B_{2g}(C) vibration.

The hydrogen vibration, A_2''(H 1), is very roughly analogous to the benzene and hexadeuterobenzene vibration, A_{2u}(H). We find in the absorption spectrum of 1 : 3 : 5-trideuterobenzene an overtone of an upper-state fundamental frequency 411 cm.$^{-1}$, which is of about the expected magnitude for the upper-state frequency A_2''(H 1). We also find in the spectrum a sequence interval 119 cm.$^{-1}$, which one would in any case be tempted to try to correlate with the sequence interval 114 cm.$^{-1}$ of the A_{2u}(H) vibration of hexadeuterobenzene.

And the frequency 119 cm.$^{-1}$, when added to the upper-state fundamental frequency 411 cm.$^{-1}$, gives correctly the known lower-state frequency of the vibration A_2''(H 1). An active overtone gives the value 531 cm.$^{-1}$ for this lower-state frequency, and it is independently known from infra-red measurements. Thus our identification of the upper-state frequency of the vibration A_2''(H 1) seems certain.

The internal spectral evidence concerning the remaining vibration A_2''(H 2) is less complete. This vibration is roughly analogous to the benzene and hexadeuterobenzene vibration B_{2g}(H). In the absorption and fluorescence spectra of 1 : 3 : 5-trideuterobenzene, we find a sequence interval of 200 cm.$^{-1}$, and an argument of exclusion (Part VI, Section 7) shows that this can only belong to the vibration A_2''(H 2). The ground-state fundamental frequency of this vibration, 915 cm.$^{-1}$, is found as an overtone in the fluorescence spectrum, and it is known from infra-red measurements. One deduces that the upper-state fundamental frequency must be 915 − 200 = 715 cm.$^{-1}$. The figure is of the expected magnitude, but the direct support which would follow from an observation of its overtone in the absorption spectrum is unfortunately not available. For a confirmatory test we have therefore to rely on the product theorem, which confirms the assignment :

$$\frac{\Pi B_{2g}A_{2u}(C_6H_6^*)}{\Pi A_2''(C_6H_3D_3^*)} = \frac{365 \times 513 \times 775}{360 \times 411 \times 715} = 1{\cdot}372 \text{ (Harmonic value} = 1{\cdot}387)$$

$$\frac{\Pi A_2''(C_6H_3D_3^*)}{\Pi B_{2g}A_{2u}(C_6D_6^*)} = \frac{360 \times 411 \times 715}{306 \times 382 \times 663} = 1{\cdot}362 \text{ (Harmonic value} = 1{\cdot}388)$$

(11) *Excited States of* 1 : 4-$C_6H_4D_2$ *and* 1 : 2 : 4 : 5-$C_6H_2D_4$. *The A_g Vibrations* (cf. Part VIII, Sections 2, 3, and 8; and Part IX, Sections 2, 3, and 8).—The six vibrations of this symmetry class correspond collectively, and to a large extent individually, to the two A_{1g} and four E_g^+ vibrations of benzene or hexadeuterobenzene. Of the six upper-state A_g fundamental frequencies of 1 : 4-dideuterobenzene, five have been directly and definitely identified in the absorption spectrum of that substance : (A_{1g}-like) 909 and 3132; (E_g^+-like) 511, 1489, and 2355 cm.$^{-1}$. Five fundamental frequencies of 1 : 2 : 4 : 5-tetradeuterobenzene have been identified with equal certainty in the corresponding spectrum : (A_{1g}-like) 895 and 2355; (E_g^+-like) 509·5, 1414, and 3133 cm.$^{-1}$. In each case the missing frequency is that of the hydrogen-bending vibration A_g(H), corresponding to the E_g^+(H 2) vibration of a D_{6h} benzene.

These missing frequencies we now calculate, using the various product ratios between the relevant frequencies of benzene, 1 : 4-dideuterobenzene, 1 : 2 : 4 : 5-tetradeuterobenzene, and hexadeuterobenzene. The results are as follows :

For 1 : 4-$C_6H_4D_2$:—$A_g(\text{H})_{\text{excited}}$ = 1075 cm.$^{-1}$

For 1 : 2 : 4 : 5-$C_6H_2D_4$:—$A_g(\text{H})_{\text{excited}}$ = 820 cm.$^{-1}$

These values may involve an error due to the circumstance that the other frequencies from which they are calculated include some which, as has been pointed out, are probably perturbed by a resonance displacement of certain upper-state energy levels. The corresponding ground-state frequency of 1: 4-dideuterobenzene is 1173·4 cm.$^{-1}$, and of 1 : 2 : 4 : 5-tetradeuterobenzene is 862·2 cm.$^{-1}$, according to the evidence of Raman spectra (Herzfeld, Hobden, Ingold, and Poole, *J.*, 1946, 379).

(12) *Excited States of* 1 : 4-$C_6H_4D_2$ *and* 1 : 2 : 4 : 5-$C_6H_2D_4$. *The A_u Vibrations* (cf. Part VIII, Sections 4 and 5; and Part IX, Sections 4 and 5).—In theory, the two A_u frequencies of excited 1 : 4-dideuterobenzene are individually identical with the upper-state E_u^+ frequencies of benzene, whilst the corresponding A_u frequencies of 1 : 2 : 4 : 5-tetradeuterobenzene are identical with the E_u^+-frequencies of excited hexadeuterobenzene. The observed exact (or very close) identity of the relevant pairs of frequencies is an important part of the basis on which the A_u frequencies are recognised in the absorption spectra of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene. We therefore expect the product theorem to be satisfied by these frequencies, as, indeed, the following figures illustrate :

$$\frac{\Pi E_u^+(C_6H_6^*)}{\Pi A_u(C_6H_4D_2^*)} = \frac{243 \times 706}{243 \times 706} = 1{\cdot}000 \text{ (Harmonic value} = 1{\cdot}000)$$

$$\frac{\Pi A_u(C_6H_4D_2^*)}{\Pi A_u(C_6H_2D_4^*)} = \frac{243 \times 706}{208 \times 591} = 1{\cdot}395 \text{ (Harmonic value} = 1{\cdot}414)$$

$$\frac{\Pi A_u(C_6H_2D_4^*)}{\Pi E_u^+(C_6D_6^*)} = \frac{208 \times 591}{208 \times 590} = 1{\cdot}002 \text{ (Harmonic value} = 1{\cdot}000)$$

(13) *Excited States of* 1 : 4-$C_6H_4D_2$ *and* 1 : 2 : 4 : 5-$C_6H_2D_4$. *The* B_{2g} *Vibrations* (cf. Part VIII, Section 6; and Part IX, Section 6).—This case is similar to the last, except that the involved symmetry classes, B_{2g} for 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene and E_g^- for benzene and hexadeuterobenzene, each contain only one vibration. The upper-state product ratios are as follows :

$$\frac{\Pi E_g^-(C_6H_6^*)}{\Pi B_{2g}(C_6H_4D_2^*)} = \frac{585}{585} = 1{\cdot}000 \text{ (Harmonic value} = 1{\cdot}000)$$

$$\frac{\Pi B_{2g}(C_6H_4D_2^*)}{\Pi B_{2g}(C_6H_2D_4^*)} = \frac{585}{452} = 1{\cdot}291 \text{ (Harmonic value} = 1{\cdot}291)$$

$$\frac{\Pi B_{2g}(C_6H_2D_4^*)}{\Pi E_g^-(C_6D_6^*)} = \frac{452}{454} = 0{\cdot}996 \text{ (Harmonic value} = 1{\cdot}000)$$

(14) *Excited States of* 1 : 4-$C_6H_4D_2$ *and* 1 : 2 : 4 : 5-$C_6H_2D_4$. *The* B_{1u} *Vibrations* (cf. Part VIII, Sections 4 and 5; Part IX, Sections 4 and 5).—This symmetry class contains one carbon and two hydrogen vibrations, collectively related to the two E_u^+, and the single A_{2u}, vibrations of benzene, and of hexadeuterobenzene. The carbon vibration, B_{1u}(C), is a close analogue of the E_u^+(C) vibration of benzene and hexadeuterobenzene; and it can readily be identified in the absorption spectra of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene by its generation of strong sequences and overtone series, closely corresponding to those given by the E_u^+(C) vibration of benzene and hexadeuterobenzene. The upper-state fundamental frequencies are 222 cm.$^{-1}$ for 1 : 4-dideuterobenzene, and 233 cm.$^{-1}$ for 1 : 2 : 4 : 5-tetradeuterobenzene. These figures are of about the estimated magnitude : they stand in the unusual numerical order, because, in this vibration, the hydrogen motion tends to concentrate in the isotope present in smaller proportion (cf. Bailey, Carson, Gordon, and Ingold, *J.*, 1946, 292).

The vibration B_{1u}(H 1) of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene is an approximate analogue of the A_{2u}(H) vibration of benzene and hexadeuterobenzene. In the absorption spectrum of 1 : 4-dideuterobenzene we find the overtone of an upper-state fundamental frequency 435 cm.$^{-1}$. This is of about the magnitude one would associate with the B_{1u}(H 1) vibration, but the spectrum itself provides no further evidence of identity. On the other hand, the absorption spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene contains the overtone of an upper-state fundamental frequency 419 cm.$^{-1}$, which is likewise of about the magnitude to be expected for the frequency of the B_{1u}(H 1) vibration; and this frequency is rather clearly identified as such by the internal evidence of the spectrum. For we find a sequence frequency, 128 cm.$^{-1}$, which, when added to the upper-state frequency 419 cm.$^{-1}$, gives correctly the known lower-state frequency, 547 cm.$^{-1}$, of the vibration B_{1u}(H 1) (Bailey, Carson, Gordon, and Ingold's infra-red observations gave 548 cm.$^{-1}$; *loc. cit.*); and one of the other combinations in which the frequency 419 cm.$^{-1}$ appears points to its belonging to the B_{1u} symmetry class.

The vibration B_{1u}(H 2) of the 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene is roughly analogous to the E_u^+(H) vibration of benzene and hexadeuterobenzene. In the absorption spectrum of 1 : 4-dideuterobenzene we find the overtone of an upper-state fundamental frequency 655 cm.$^{-1}$. The absorption spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene yields similar evidence of an upper-state fundamental frequency 665 cm.$^{-1}$. In each case the frequency is of about the magnitude we should expect for the vibration B_{1u}(H 2), the order of the two frequencies again being explicable by the concentration of much of the hydrogen motion in the isotope present in smaller proportion (*idem, ibid.*). But in neither case does the spectrum itself yield any further evidence of the identity of the frequencies. The main support for our assignments of these upper-state frequencies to the vibration B_{1u}(H 2), and of the upper-state frequency 435 cm.$^{-1}$ of 1 : 4-dideuterobenzene to the vibration B_{1u}(H 1), is therefore that these three initially tentative assignments, in combination with the three secure B_{1u} assignments already mentioned, give correct B_{1u} frequency products for both excited 1 : 4-dideuterobenzene and excited 1 : 2 : 4 : 5-tetradeuterobenzene. The following product ratios establish this :

$$\frac{\Pi E_u^+ A_{2u}(C_6H_6^*)}{\Pi B_{1u}(C_6H_4D_2^*)} = \frac{243 \times 513 \times 706}{222 \times 435 \times 655} = 1{\cdot}391 \text{ (Harmonic value} = 1{\cdot}396)$$

$$\frac{\Pi B_{1u}(C_6H_4D_2^*)}{\Pi B_{1u}(C_6H_2D_4^*)} = \frac{222 \times 435 \times 655}{233 \times 419 \times 665} = 0{\cdot}974 \text{ (Harmonic value} = 0{\cdot}988)$$

$$\frac{\Pi B_{1u}(C_6H_2D_4^*)}{\Pi E_u^+ A_{2u}(C_6D_6^*)} = \frac{233 \times 419 \times 665}{208 \times 382 \times 590} = 1{\cdot}385 \text{ (Harmonic value} = 1{\cdot}396)$$

(15) *Excited States of* 1 : 4-$C_6H_4D_2$ *and* 1 : 2 : 4 : 5-$C_6H_2D_4$. *The* B_{2u} *Vibrations* (cf. Part VIII, Section 7; and Part IX, Section 7).—This symmetry class possesses one carbon and two

hydrogen vibrations. They are collectively related to the two B_{2g}, and the single E_g^-, vibrations of benzene and hexadeuterobenzene. The carbon vibration is quite a close analogue of the vibration B_{2g}(C) of benzene and hexadeuterobenzene. In the absorption spectra of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene, we find, as overtones, the upper-state fundamental frequencies 357 cm.$^{-1}$ and 351 cm.$^{-1}$, respectively. Both are of about the expected magnitude for the vibration B_{2g}(C); and they could hardly belong to any other fundamental vibration.

The absorption spectra of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene also contain overtones of the upper-state fundamental frequencies 457 cm.$^{-1}$ and 535 cm.$^{-1}$, respectively. Each is of about the magnitude to be expected of the lower of the two B_{2g} hydrogen frequencies in each excited molecule. But the respective spectra provide no additional evidence of the identity of these frequencies.

The same situation prevails in relation to the higher of the B_{2g} hydrogen frequencies. The absorption spectra of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene contain overtones of the upper-state fundamental frequencies 775 cm.$^{-1}$ and 649 cm.$^{-1}$, respectively. Each of these is of about the expected magnitude, but the spectra yield no further evidence of identity. The one additional check which we have is that, for each compound, the two initially provisional assignments, in combination with the secure assignment of the carbon frequency, give a correct B_{2g} frequency product. This is established by the following product ratios for the upper electronic state :

$$\frac{\Pi B_{2g}E_g^-(C_6H_6^*)}{\Pi B_{2g}(C_6H_4D_2^*)} = \frac{365 \times 585 \times 775}{357 \times 457 \times 775} = 1{\cdot}309 \text{ (Harmonic value} = 1{\cdot}326)$$

$$\frac{\Pi B_{2g}(C_6H_4D_2^*)}{\Pi B_{2g}(C_6H_2D_4^*)} = \frac{357 \times 457 \times 775}{351 \times 535 \times 649} = 1{\cdot}038 \text{ (Harmonic value} = 1{\cdot}031)$$

$$\frac{\Pi B_{2g}(C_6H_2D_4^*)}{\Pi B_{2g}E_g^-(C_6D_6^*)} = \frac{351 \times 535 \times 649}{306 \times 454 \times 663} = 1{\cdot}323 \text{ (Harmonic value} = 1{\cdot}331)$$

(15) *Excited State of* C_6H_5D. *The* A_2 *Vibrations* (cf. Part X, Sections 4 and 6).—According to theory, the three upper-state A_2 frequencies of monodeuterobenzene are individually identical with the two E_u^+, and the single E_g^-, frequencies of excited benzene, and also with the two A_u, and the single B_{2g}, frequencies of excited 1 : 4-dideuterobenzene. Naturally, the relevant product ratios are unity. Two of the three monodeuterobenzene frequencies, 243 and 585 cm.$^{-1}$, can be found and identified in the absorption spectrum of that substance : the values are just those we expect. The third has not been so identified, but we know its value from its identified equivalents in the spectra of the two isotopically isomeric compounds. Another form of the same statement is that we can calculate the missing frequency from the observed frequencies and the product theorem :

$$\text{For } C_6H_5D :— A_2(H)_{\text{excited}} = 706 \text{ cm.}^{-1}$$

The corresponding frequency of the electronic ground state is 970 cm.$^{-1}$ (Herzfeld, Ingold, and Poole, *loc. cit.*).

(16) *Excited State of* C_6H_5D. *The* B_2 *Vibrations* (cf. Part X, Sections 4, 5, 6, and 7).—This symmetry class contains two carbon and four hydrogen vibrations, collectively corresponding to the six out-of-plane vibrations of benzene. Four of the upper-state frequencies of monodeuterobenzene, those of the vibrations which correspond more or less nearly to the benzene vibrations E_u^+(C), B_{2g}(C), A_{2u}(H), and E_g^-(H), can be not only found, but also identified with fair certainty, in the absorption spectrum of monodeuterobenzene. Two other frequencies are found which can be assigned to the remaining vibrations, namely, those vibrations which are most closely allied to the benzene vibrations E_u^+(H) and B_{2g}(H). The frequencies have the approximate magnitudes to be expected for upper-state frequencies thus assigned, but the spectrum offers no further evidence of their identity. In adopting the assignments suggested, we therefore rely on the circumstance that these two frequencies, in conjunction with the four more securely assigned frequencies already mentioned, produce the correct frequency product for the B_2 symmetry class of excited monodeuterobenzene. This is established by the following product ratios *inter alia* :

$$\frac{\Pi E_u^+ B_{2g} A_{2u} E_g^-(C_6H_6^*)}{\Pi B_2(C_6H_5D^*)} = \frac{243 \times 365 \times 513 \times 585 \times 706 \times 775}{230 \times 360 \times 476 \times 552 \times 690 \times 720} = 1{\cdot}348 \text{ (Harmonic value} = 1{\cdot}359)$$

$$\frac{\Pi B_2(C_6H_5D^*)}{\Pi B_{1u}B_{2g}(C_6H_4D_2^*)} = \frac{230 \times 360 \times 476 \times 552 \times 690 \times 720}{222 \times 357 \times 435 \times 457 \times 655 \times 775} = 1{\cdot}351 \text{ (Harmonic value} = 1{\cdot}362)$$

$$\frac{\Pi B_2(C_6H_5D^*)}{\Pi E''A_2''(C_6H_3D_3^*)} = \frac{230 \times 360 \times 476 \times 552 \times 690 \times 720}{223 \times 360 \times 411 \times 475 \times 680 \times 715} = 1{\cdot}360 \text{ (Harmonic value} = 1{\cdot}375)$$

(17) *Partial Summary.*—This section completes the theoretical basis of our assignments of frequencies to the upper-state vibrations of the planar symmetry classes A_{1g}, B_{1u}, and E_g^+ of benzene and hexadeuterobenzene, and of the corresponding symmetry classes of the partly deuterated benzenes studied. It also extends, though it does not complete, the theoretical arguments on which we rely in our assignments of frequencies to all the out-of-plane vibrations of the upper electronic states of the benzenes studied, *i.e.*, the vibrations of the symmetry classes A_{2u}, B_{2g}, E_u^+ and E_g^- of benzene and hexadeuterobenzene, and of the related symmetry classes of the partly deuterated benzenes.

Two matters therefore remain to be treated. The first need is to complete the discussion of the upper-state out-of-plane vibrations. The second is to consider the upper-state planar vibrations of those symmetry classes of benzene and hexadeuterobenzene which have been left aside hitherto, *viz.*, the three symmetry classes A_{2g}, B_{2u}, and E_u^-. These are the subjects of the following Section.

(B) *Force System for the Excited State.*

(1) *The Wilson–Bell Potential-energy Function for Benzene.*—The simplest normal co-ordinate treatment which has been applied to the benzene molecule is that of Wilson (*Physical Rev.*, 1934, **45**, 706), who adopted a valency-force potential-energy function containing six constants, and from this derived a complete set of equations for the twenty fundamental frequencies in terms of the six constants. Wilson's function may be written thus :

$$2V = F\Sigma r^2 + f\Sigma s^2 + D\Sigma a^2\rho^2 + d\Sigma b^2\sigma^2 + G\Sigma c^2\phi^2 + g\Sigma b^2\mu^2 \quad . \quad . \quad . \quad (1)$$

Here V is the potential energy of deformation of the molecule; r, s, ρ σ, ϕ, and μ are the geometrical variables in terms of which the deformation is expressed; F, f, D, d, G, and g are the force-constants (Kohlrausch's notation); and a, b, and c are geometrical constants. The geometrical variables are defined as follows : r is the deviation of the length of a C–C bond, and s of that of a C–H bond, from their respective equilibrium lengths; ρ is the angular deformation of an internal ring angle, and σ is the angular deviation, in the plane of the ring, of a C–H bond from the bisector of an external ring angle; ϕ is the angle through which a C–C bond is twisted by out-of-plane displacements of the carbon atoms attached to the atoms forming the bond, and μ is the angle by which the bond of a hydrogen atom is bent out of the plane of the nearest three carbon atoms. The force-constants correspond : F is the carbon-stretching, and f is the hydrogen-stretching, constant, and D is the carbon-bending, and d the hydrogen-bending, constant, all with reference to motion in the plane of the molecule; whilst G is the carbon-twisting, and g the hydrogen-bending, constant, both relating to out-of-plane motion. The geometrical constants have the following meanings : a is the equilibrium C–C bond-length, and b is the equilibrium C–H bond-length, whilst c is an abbreviation for $\sqrt{3}a/2$. Each summation extends over six similar terms, one for each of six like atoms or six like bonds.

It is not necessary to quote the frequency equations which follow from equation (1). There are ten, one for each of the ten symmetry classes which possess vibrations, the order of each equation, and the number of its roots, corresponding to the number of frequencies belonging to the symmetry class. The equations are separable into two sets : the six which give the fourteen planar frequencies involve only the force-constants F, f, D, and d; whilst the four which give the six out-of-plane frequencies involve only the force-constants G and g.

These equations have been compared with spectrally determined frequencies for the electronic ground states of benzene and hexadeuterobenzene by Kohlrausch (*Z. physikal. Chem.*, 1935, **30**, 307) and Lord and Andrews (*J. Physical Chem.*, 1937, **41**, 149); and further spectral data have since become available for the comparison. As regards the planar frequencies, there are no discrepancies greater than 17% : here the agreement seems to be about as good as one should expect for a potential function without cross terms. But for the out-of-plane vibrations, the discrepancies are much greater, ranging up to 50%. However, Bell (*Trans. Faraday Soc.*, 1945, **41**, 293) has proposed to modify equation (1) in a manner which not only is physically very reasonable, but also has the effect of making the out-of-plane portion of the potential energy function at least as successful as the in-plane portion. He remarks that it cannot be right to take into account only the effect, on the twisting of a C–C bond, of the out-of-plane displacements of the two carbon atoms attached to the atom-pair, neglecting the similar effect of the out-of-plane displacements of the two hydrogen atoms. He observes that, if only one torsional force-constant is to be used, the best measure of the torsion about a given C–C bond is $\phi_C + \phi_H$, where ϕ_C and ϕ_H are the relative angular twists, about the given bond, of the two attached C–C bonds and the two attached C–H bonds, respectively. This modifies the potential-energy

function, and leads to a new set of equations for the out-of-plane frequencies. Bell has given these equations, and has shown that they satisfactorily represent the out-of-plane frequencies of the ground state of benzene.

In calculating relationships between the fundamental frequencies of the electronically excited states of benzene and hexadeuterobenzene, and in comparison calculations on the electronic ground states of these molecules, we have accordingly used Bell's equations for the out-of-plane frequencies and Wilson's equations for the planar frequencies, the complete potential energy function being $V = V_o + V_p$, where

$$2V_o = Q\Sigma c^2(\phi_C + \phi_H)^2 + g\Sigma b^2\mu^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$2V_p = F\Sigma r^2 + f\Sigma s^2 + D\Sigma a^2\rho^2 + d\Sigma b^2\sigma^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The constant Q is the new torsional force-constant, which takes into account the twisting of a carbon bond by the motion of the hydrogen atoms as well as by the motion of other carbon atoms. The physical data employed in the calculations, apart from universal constants, are the isotopic weights, H = 1·008, D = 2·014, and C = 12·00, and the internuclear distances, C–C = 1·39 A. and C–H = 1·08 A. for the ground state, and C–C = 1·43 A. and C–H = 1·07 A. for the excited state (cf. Part XII).

(2) *Excited States of* C_6H_6 *and* C_6D_6. *The Out-of-plane Vibrations* (cf. Section A, Sub-sections 5, 6, 7, and 8).—The two out-of-plane vibrations for the assignments of upper-state frequencies to which the strongest cases can be presented, purely on the internal evidence of the absorption and fluorescence spectra of benzene and hexadeuterobenzene, are the vibrations E_u^+(C) and E_g^-(H). It was therefore an obvious step to employ these frequencies, either of benzene or of hexadeuterobenzene, in order to determine the force-constants Q and g of equation (2), and from these to calculate the remaining out-of-plane frequencies of the upper electronic states of the two molecules. It makes little difference which of the pairs of frequencies we employ initially, and the results of a calculation, in which we have started from the two hexadeuterobenzene frequencies, are shown in the upper part of Table II.

As a control, a similar calculation starting from the corresponding pair of frequencies of hexadeuterobenzene in the electronic ground state, has been carried through for the ground states of benzene and hexadeuterobenzene. The results are given in the lower part of Table II. In both parts of the Table, the columns headed " Obsd." contain the spectrally determined frequencies, whilst the columns headed " Corrn." record the percentage corrections which would convert the calculated frequencies into the spectrally determined values.

TABLE II.

Calculated Out-of-plane Frequencies (cm.$^{-1}$) for Excited and Normal Benzene and Hexadeuterobenzene. Comparison with Spectrally Observed Values.

(a) *Excited state.*

Starting frequencies: those marked * below.
Force constants: Q = 2090 dynes/cm., and g = 12500 dynes/cm.

	Benzene.			Hexadeuterobenzene.		
Vibration.	Calc.	Obsd.	Corrn., %.	Calc.	Obsd.	Corrn., %.
A_{2u}(H)	478	513	+ 7·3	351	382	+ 8·8
B_{2g}(C)	387	365	− 5·7	328	306	− 6·7
B_{2g}(H)	774	775	+ 0·1	637	663	+ 4·1
E_g^-(H)	585	585	± 0·0	—	454 *	—
E_u^+(C)	238	243	+ 2·1	—	208 *	—
E_u^+(H)	726	706	− 2·8	588	590	+ 0·3

(b) *Ground state.*

Starting frequencies: those marked † below.
Force constants: Q = 6700 dynes/cm., and g = 22900 dynes/cm.

	Benzene.			Hexadeuterobenzene.		
Vibration.	Calc.	Obsd.	Corrn., %.	Calc.	Obsd.	Corrn., %.
A_{2u}(H)	646	671	+ 3·9	475	496·5	+ 4·1
B_{2g}(C)	638	703	+10·2	572	601	+ 5·1
B_{2g}(H)	1136	985	−12·4	898	827	− 7·9
E_g^-(H)	851	849	− 0·2	—	662 †	—
E_u^+(C)	390	405	+ 3·8	—	352 †	—
E_u^+(H)	1075	970	− 9·8	844	793	− 6·0

The general agreement between the calculated upper-state frequencies and those assigned on the basis of the spectral observations is evidently satisfactory. In particular the assignments of the A_{2u}(H) and B_{2g}(C) frequencies are confirmed. Since the calculations were used in order roughly to locate the E_u^+(H) and B_{2g}(H) frequencies, prior to their identification in the spectra, these frequencies automatically agree with the calculated values.

We have carried out similar calculations starting from the well-established upper-state E_u^+(C) frequency of either benzene or hexadeuterobenzene and a second upper-state frequency given by the use of some trial assignment in place of the adopted assignment of the E_g^- frequency. For instance, one of our earlier ideas was that the fairly strong sequence frequencies, 265 cm.$^{-1}$ of benzene and 208 cm.$^{-1}$ of hexadeuterobenzene, which we now assign to the vibration E_g^-(H) might belong to the vibration B_{2g}(C). But either of the upper-state B_{2g}(C) frequencies of benzene and hexadeuterobenzene, which would then follow, produces quite absurd results when, in combination with the E_u^+(C) frequency, it is made the basis of a calculation such as that illustrated above. We have been unable to find any scheme, other than that now proposed, of spectral assignments to out-of-plane vibrations of the upper electronic state, which is consistent both with the product rule and with the force-field calculations. This completes our case for the out-of-plane assignments.

(3) *Excited States of* C_6H_6 *and* C_6D_6. *The* A_{2g}, B_{2u}, *and* E_u^- *Planar Vibrations.*—Our application of force-field calculations to the determination of planar vibration frequencies of the upper electronic states of benzene and hexadeuterobenzene has followed different lines from those already illustrated, because of the different situation prevailing with regard to the planar vibrations. On the one hand, the upper-state frequencies of all the vibrations of the planar symmetry classes A_{1g}, B_{1u}, and E_g^+ have already been determined with greater certainty and precision than could have been achieved by force-field calculations. On the other hand, we as yet know nothing about any of the upper-state vibration frequencies of the other three planar symmetry classes, A_{2g}, B_{2u}, and E_u^-. Therefore, as an initial step towards the evaluation of these frequencies of excited benzene and hexadeuterobenzene, we first used the known planar frequencies of the upper electronic states of these molecules in order to determine the force constants, F, f, D, and d, of equation (3), and then employed these constants for the calculation of the unknown planar frequencies.

The calculation was carried out as follows. First, the carbon- and hydrogen-stretching force-constants, F and f, were derived from the upper-state A_{1g} frequencies. With the aid of these constants, a mean value of the carbon-bending constant, D, was then calculated from the upper-state B_{1u} frequencies and the E_g^+ frequencies, in the latter case by the use of those coefficients in the frequency equation which give the sum and product of the squares of the four frequencies. Then, with the aid of these three constants, a value of the hydrogen-bending constant, d, was derived from the upper-state E_g^+ frequencies, employing for this purpose the expression for the product of the squares of the frequencies. The above procedures were carried through independently for benzene and hexadeuterobenzene, with the results shown in the upper left-hand part of Table III. The consistency is good for F and f, but poor for D and d. The mean values listed were used for the calculation of those upper-state frequencies which are entered under the heading " Calc." in the top right-hand part of Table III. The significance of the adjacent figures under the heading " E.A." is explained below.

As a control on the values thus obtained, the calculation was repeated for the electronic ground states of benzene and hexadeuterobenzene. The resulting force-constants are given in the lower left-hand portion of Table III. These force-constants are almost certainly not the best that could be obtained by making use of all that is known about the frequencies of benzene and hexadeuterobenzene in their electronic ground states. However, we particularly wanted values which would be comparable to those obtained for the upper electronic state, and subject to similar errors. As before, we used mean values for the calculation of the frequencies of both molecules. These frequencies are contained in the columns headed " Calc." in the lower right-hand part of the Table. We are able to compare them with values derived from spectral observations, and such values, taken from Herzfeld, Ingold, and Poole's list (*J.*, 1946, 332), are given in the neighbouring columns headed " Obsd.". The deviations, entered in the columns headed " Corrn.", are expressed as the percentage corrections which would have to be applied to the calculated frequencies in order to produce the observed values.

Our object in making the frequency calculations for the electronic ground state was to obtain a set of correction factors, with the aid of which we might hope to improve our estimates of the A_{2g}, B_{2u}, and E_u^- frequencies of benzene and hexadeuterobenzene in their electronically excited states. It is true that, as one sees from Table II, there is no very close correspondence between

TABLE III.

Some Calculated Planar Frequencies (cm.$^{-1}$) of Excited and Normal Benzene and Hexadeuterobenzene. Comparison of Calculated Ground-state Frequencies with Spectrally Determined Values.

(a) *Excited state.*

[Starting frequencies: those of A_{1g}, B_{1u}, and E_g^+ symmetry classes given in Table V.]

Force constants.

(F, f, D and d in dynes/cm.).

	C_6H_6.	C_6D_6.	Mean.
10^{-5} F	6·54	6·53	6·53
10^{-5} f	5·30	5·40	5·35
10^{-5} D	0·58	0·46	0·52
10^{-5} d	0·50	0·64	0·57

Frequencies (cm.$^{-1}$).

	C_6H_6.		C_6D_6.	
Vibration.	Calc.	E.A.	Calc.	E.A.
A_{2g}(H)	1103	1210	857	940
B_{2u} (C)	1700	1510	1668	1440
B_{2u} (H)	961	1010	683	750
E_u^- (C)	1632	1470	1697	1320
E_u^- (H 1)	1024	940	754	740
E_u^- (H 2)	2984	3130	2025	2300

(b) *Ground state.*

[Starting frequencies: those of A_{1g}, B_{1u}, and E_g^+ symmetry classes given in *J.*, 1946, 332.]

Force constants

(F, f, D, and d in dynes/cm.).

	C_6H_6.	C_6D_6.	Mean.
10^{-5} F	7·65	7·58	7·61
10^{-5} f	5·02	5·10	5·06
10^{-5} D	0·77	0·59	0·68
10^{-5} d	0·60	0·79	0·69

Frequencies (cm.$^{-1}$).

	C_6H_6.			C_6D_6.		
Vibration.	Calc.	Obsd.	Corrn., %.	Calc.	Obsd.	Corrn., %.
A_{2g}(H)	1214	1326	+ 9·1	942	1037	+ 10·1
B_{2u} (C)	1837	1648	− 10·3	1833	1571	− 14·3
B_{2u} (H)	1053	1110	+ 5·4	750	825	+ 10·0
E_u^- (C)	1734	1485	− 14·3	1638	1333	− 18·4
E_u^- (H 1)	1118	1037	− 7·3	838	813	− 3·0
E_u^- (H 2)	2870	3080	+ 7·3	2130	2294	+ 7·7

the correction factors applying to the different out-of-plane vibrations in the two electronic states. All that can be said is that the order of magnitude of the deviations between the calculated and observed frequencies of these vibrations is the same for both states, and that, on the whole, the errors for the upper state are smaller than for the lower. On the other hand, in the case of the planar vibrations, it seems reasonable to assume a much closer correlation between the errors involved in the calculation of corresponding frequencies of the two electronic states—for two reasons. The first is that, whereas the force-constants for the out-of-plane vibrations are greater by factors of two and three in the electronic ground state than in the excited state, the force-constants for the planar vibrations differ by less than 25% in the two states; which therefore behave as much more closely similar dynamical systems with respect to planar vibrations than they do with respect to out-of-plane vibrations. The second reason is that, although the determined values of the planar force-constants are not all independent of whether they are obtained from the frequencies of benzene or from those of hexadeuterobenzene, the percentage deviations between the values obtained in these two ways for the electronic ground state are repeated very closely in the values applying to the excited state. Therefore we presume that the errors inherent in our calculations of the planar frequencies are similar for the two electronic states; so that we may expect generally to improve our estimates of those planar frequencies which cannot be directly observed, by applying to the calculated values correction factors deduced from a comparison of similarly calculated ground-state frequencies with data derived from spectral observation.

Several other empirical, or partly empirical, guides to the upper-state frequencies of the symmetry classes A_{2g}, B_{2u}, and E_u^- are available. A comparison of the frequencies, in the lower and upper electronic states, of those vibrations of benzene and hexadeuterobenzene, whose frequencies in the upper state are most closely and definitely determined by spectral observation, shows that the percentage drop of frequency, which a given vibration undergoes when the molecule is electronically excited, is essentially a characteristic of the vibration, and is nearly independent of whether the frequencies belong to benzene or to hexadeuterobenzene. Only a partial explanation of this effect can be given in simple terms, but its reality, which the figures of Table IV illustrate, cannot be doubted. This, then, is one guide; for we should certainly expect those frequencies which we are not able directly to observe, to conform to the rule which all the other frequencies follow.

Again we know empirically, and there is also a theoretical explanation of the fact, that, for

a given electronic system, all protium-stretching frequencies lie within a certain narrow range, whilst all deuterium-stretching frequencies lie within another narrow range. These frequency ranges of the upper electronic state are well defined by the spectral observations, not only on benzene and hexadeuterobenzene, but also on all the partly deuterated benzenes. The symmetry class E_u^- of benzene and hexadeuterobenzene contains a hydrogen-stretching vibration, and we may expect its frequencies to conform to the general rule.

Finally, the upper-state frequencies of each of those symmetry classes, A_{2g}, B_{2u}, and E_u^-, of benzene and hexadeuterobenzene with which we are concerned must satisfy the product theorem.

TABLE IV.

Percentage Reduction undergone by Some Fundamental Frequencies (cm.$^{-1}$) of Benzene and Hexadeuterobenzene on Electronic Excitation.

	A_{1g}.		E_g^+.			
C_6H_6 (ground state)	992	3062	606	3047	1596	1178
C_6H_6 (excited state)	923	3130	521	3080	1470	1130
% Drop (C_6H_6)	7·0	− 2·2	14·0	− 1·1	7·9	4·9
C_6D_6 (ground state)	943	2293	577	2265	1551	867
C_6D_6 (excited state)	879	2340	499	2320	1403	830
% Drop (C_6D_6)	7·3	−2·2	15·7	−2·5	9·5	4·3

	A_{2u}.	B_{2g}.		E_u^+.		E_g^-.
C_6H_6 (ground state)	671	703	985	405	970	849
C_6H_6 (excited state)	513	365	775	243	706	585
% Drop (C_6H_6)	23·6	48·0	21·3	40·0	27·2	31·1
C_6D_6 (ground state)	496	601	827	352	793	662
C_6D_6 (excited state)	382	306	663	208	590	454
% Drop (C_6D_6)	23·0	49·0	19·8	40·9	25·6	31·4

It seemed desirable to offer, for those upper-state vibrations of benzene and hexadeuterobenzene on which we have no direct spectral information, a set of frequencies which have been fixed as closely as possible with the aid of our empirical, as well as theoretical, resources; and that is why, alongside of the calculated frequencies given in the top right-hand section of Table III, two further columns of figures, headed " E.A.", have been added. The heading means that they are empirically adopted frequencies, which we have fixed as described above, in the first stage roughly, by adjusting the crude, calculated values with the aid of parallel calculations on the ground state, and then more closely by reference to the indications or requirements of all the guiding rules mentioned. The figures are given in rounded form, for, though it is difficult to estimate their accuracy, it would clearly be inappropriate to quote units. However, they satisfy all the tests we are able to apply, including one to be considered in Part XII.

(C) *Summary of Fundamental Frequencies of Excited Benzenes.*

Having now exploited most of the methods by which it seems possible to extract, from observations on the ultraviolet absorption and fluorescence spectra of the various isotopically isomeric benzenes, information about their fundamental vibration frequencies in the upper electronic state, we give, in Tables V and VI, a conspectus of the determined frequencies. Two tables are necessary in order to show how the values shift with the different modes of isotopic substitution. This is because the symmetry of benzene and hexadeuterobenzene can be degraded to that of monodeuterobenzene either by way of the symmetry of 1 : 3 : 5-trideuterobenzene, or through that of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene; and the vibrations group themselves in different ways, and their symmetry classes coalesce in different patterns, according to the route taken.

Many interesting effects of isotopic substitution can be seen amongst these frequencies of the upper electronic state. However, we omit discussion of this matter, because it would be lengthy, and because much of the argument runs parallel to that which has already been fully given with reference to the effects of isotopic substitution on the vibration frequencies of the same molecules in their electronic ground states (*J.*, 1946, 222, *et seq.*). It is thought that the following pages from the papers cited, if read in conjunction with the present Tables, will furnish a sufficient indication of what might have been written about the forms of the vibrations which the excited electronic system controls, and about the ways in which they modify one another when the molecule is loaded with extra neutrons in the different ways studied: *loc. cit.*,

pp. 259—265, 268 and 269, 278 and 279, 284—287, 292 and 293, 298 and 299, 312, and 315. It is to be noted that some rather marked differences are exhibited in this connexion between the two electronic states in relation to their out-of-plane vibrations.

The frequencies which appear in Roman type in Tables V and VI, without any added indications, are those which are based directly on spectral observations, and on well-supported assignments of the observed bands. The frequencies which are printed in Roman type in parentheses are also based on observed bands, but with assignments which, so far as the internal spectral evidence is concerned, are still somewhat provisional, though they are supported by theoretical considerations, including some mentioned in Part XII. The frequencies printed in italics, without an additional indication, are calculated from related observed frequencies with the help of the product rule. The italicised frequencies in parentheses are deduced from observed vibration frequencies by consideration of the relevant normal co-ordinates. Finally, the italicised figures in square brackets are the frequencies which have been obtained by a combination of calculation and the application of partly empirical rules, as described above.

TABLE V.

Correlation of Fundamental Frequencies (cm.$^{-1}$) of the Upper Electronic State ($\mathbf{B}_{2u}$) of Benzenes of the Symmetry Types D_{6h}, D_{3h}, and C_{2v}.

Description of vibration.	D_{6h}.			D_{3h}.		C_{2v}.	
	Class.	C_6H_6.	C_6D_6.	Class.	$C_6H_3D_3$.	Class.	C_6H_5D.
C-stretching	A_{1g}	923	879	A_1'	893	A_1	920
H-stretching		3130	*2340*		3135		3129
C-bending	B_{1u}	*985*	*940*		988		990
H-stretching		(*3130*)	(*2340*)		2300		3081
C-bending	E_g^+	521	499	E'	513		517
H-stretching		3080	2320		3085		2348
C-stretching		1470	1403		1428		1472
H-bending		*1130*	(830)		(824)		—
C-deformation	E_u^-	[*1470*]	[*1320*]		—		—
H-bending		[*940*]	[*740*]		—		—
H-stretching		[*3130*]	[*2300*]		2330		—
Out-of-plaue	E_u^+	243	208	E''	223	A_2	243
Out-of-plane		706	590		680		(*706*)
Out-of-plane	E_g^-	585	454		495		585
H-bending	A_{2g}	[*1210*]	[*940*]	A_2'	—	B_1	—
C-stretching	B_{2u}	[*1510*]	[*1440*]		—		—
H-bending		[*1010*]	[*750*]		—		—
C-bending	E_g^+	521	499	E'	513		517
H-stretching		3080	2320		3085		3072
C-stretching		1470	1403		1428		1446
H-bending		*1130*	(830)		(824)		—
C-deformation	E_u^-	[*1470*]	[*1320*]		—		—
H-bending		[*940*]	[*740*]		—		—
H-stretching		[*3130*]	[*2300*]		2330		—
Out-of-plane	A_{2u}	513	382	A_2''	411	B_2	476
Out-of-plane	B_{2g}	365	306		360		360
Out-of-plane		775	663		715		720
Out-of-plane	E_u^+	243	208	E''	223		230
Out-of-plane		706	590		680		690
Out-of-plane	E_g^-	585	454		495		552

TABLE VI.

Correlation of Fundamental Frequencies (cm.$^{-1}$) of the Upper Electronic State (B_{2u}) of Benzenes of the Symmetry Types D_{6h}, V_h, and C_{2v}.

Description of vibration.	D_{6h}.			V_h.			C_{2v}.	
	Class.	C_6H_6.	C_6D_6.	Class.	$C_6H_4D_2$.	$C_6H_2D_4$.	Class.	C_6H_5D.
C-stretching	A_{1g}	923	879	A_g	909	895	A_1	920
H-stretching		3130	*2340*		3132	2355		3129
C-bending	E_g^+	521	499		511	509·5		517
H-stretching		3080	2320		2355	3133		2348
C-stretching		1470	1403		1489	1414		1472
H-bending		*1130*	(830)		*1075*	*820*		—
C-bending	B_{1u}	*985*	*940*	B_{2u}	—	—		990
H-stretching		(*3130*)	(*2340*)		—	—		3081
C-deformation	E_u^-	[*1470*]	[*1320*]		—	—		—
H-bending		[*940*]	[*740*]		—	—		—
H-stretching		[*3130*]	[*2300*]		—	—		—
Out-of-plane	E_u^+	243	208	A_u	243	208	A_2	243
Out-of-plane		706	590		706	591		(*706*)
Out-of-plane	E_g^-	585	454	B_{2g}	585	452		585
H-bending	A_{2g}	[*1210*]	[*940*]	B_{1g}	—	—	B_1	—
C-bending	E_g^+	521	499		516·5	505		517
H-stretching		3080	2320		3075	2333		3072
C-stretching		1470	1403		1469	1414		1446
H-bending		*1130*	(830)		—	—		—
C-stretching	B_{2u}	[*1510*]	[*1440*]	B_{2u}	—	—		—
H-bending		[*1010*]	[*750*]		—	—		—
C-deformation	E_u^-	[*1470*]	[*1320*]		(787)	—		—
H-bending		[*940*]	[*740*]		—	—		—
H-stretching		[*3130*]	[*2300*]		—	—		—
Out-of-plane	A_{2u}	513	382	B_{1u}	435	419	B_2	476
Out-of-plane	E_u^+	243	208		222	233		230
Out-of-plane		706	590		655	665		690
Out-of-plane	B_{2g}	365	306	B_{2g}	357	351		360
Out-of-plane		775	663		775	649		720
Out-of-plane	E_g^-	585	454		457	535		552

In our opinion, the most uncertain of all these frequencies are those of the B_{2u} C-stretching vibration of benzene and hexadeuterobenzene. From their mode of derivation, these two upper-state frequencies are almost bound proportionally to reproduce any considerable error that may affect Herzfeld, Ingold, and Poole's values of the corresponding ground-state frequencies. As these authors emphasized, their assignment of frequencies to the B_{2u}(C) vibration rests on an argument of such a kind that the possibility of error cannot be excluded.

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106. *Excited States of Benzene. Part XII. The Effect of an Electronic Excitation on the Geometry, Elastic Properties, and Zero-point Energy of the Benzene Molecule: and the Effect of Isotopic Substitution on the Transition Energy.*

By Francesca M. Garforth, Christopher K. Ingold, and Harry G. Poole.

Section A.—Conclusions concerning the geometry and dynamics of the first excited state of benzene are derived from the spectroscopic observations and considerations presented in the preceding papers.

The excited molecule has the full symmetry of a plane regular hexagon, but the C–C bonds are found to have expanded by 2·5% (from 1·39 A. to 1·43 A.), and the C–H bonds to have contracted by 1·0% (from 1·08 A. to 1·07 A.), in the course of the electronic excitation. These geometrical changes can be qualitatively understood on the well-established basis that the optical electron comes from the unsaturation shell. Its promotion produces a new orbital node, intersecting the geometrical bonds of the carbon ring, and thus decreases the bonding properties of the shell. Its excitation also increases the effective nuclear charge and unsaturation of the carbon atoms (which thus experience the beginnings of the development of carbonium ion character), and this shortens those bonds in which the unsaturation electrons do not participate.

The C–C stretching force-constant drops by 14% in the course of the electronic excitation, the bonds thus losing a considerable proportion of that part of their resistance to stretching which they derive from the bonding properties of the unsaturation electrons. The C–H stretching force-constant simultaneously increases by 6%. The electronic explanation of these dynamical changes closely corresponds to that of the associated geometrical changes.

The two elastic constants used to measure the resistance to angular deformation, in the plane of the molecule, of the three bonds of any one carbon atom drop substantially in the electronic excitation. Part of this form of resistance to deformation is not due to the unsaturation electrons: it would be there if they were removed, making every carbon atom a carbonium ion. The part which is due to the unsaturation electrons, and which therefore suffers reduction during the excitation, arises in three ways, *viz.*, by the repulsions exerted by the unsaturation electrons on the various saturated electron-pairs, by the shortening effect of the unsaturation electrons on the carbon bonds, with resulting increase in the repulsions between the saturated electron-pairs, and by the repulsion between the spin-coupled pairs of the unsaturation shell itself. All three effects act on the carbon-angle constant, which diminishes by 23%, but only the first two influence the hydrogen-angle constant, which drops by 17%, in the course of the electronic excitation.

Resistance to out-of-plane deformation is affected much more drastically by the electronic excitation, because such resistance comes almost entirely from the unsaturation shell. An elastic constant associated with the twisting of C–C bonds is reduced by 68%, and a constant connected with the out-of-plane bending of C–H bonds is diminished by 45%. The effect on the twisting constant is due partly to the increase of anti-bonding properties within the unsaturation shell, and partly also to the reduction of the non-bonding repulsions between the shell and other electron pairs. The effect on the out-of-plane bending constant is due essentially to the diminution in the non-bonding repulsions.

Section B.—The position of the electronic origin of the transition studied is not the same for the different isotopic forms of benzene: successive deuteration shifts the origin steadily towards the far-ultraviolet.

The energy of an electronic transition consists, not merely of the difference of electronic energy in the combining states, but of this plus the difference of nuclear-zero-point energy. In the case of benzene and hexadeuterobenzene, we know the vibration frequencies completely enough to be able to calculate the zero-point energy; and it turns out that, in relation to the energy of the electronic transition, the zero-point energy of these molecules is very substantial, being about one-half as large as the purely electronic part of the transition energy. The position of the electronic origin is thus considerably affected by the zero-point energy difference.

The isotope shift of the electronic origin is in principle the sum of the isotopic shifts in the purely electronic transition energy, and in the nuclear-zero-point transition energy. The former effect is negligible in relation to the observed shift, which amounts to 200 cm.$^{-1}$ from benzene to hexadeuterobenzene. This shift can be explained quantitatively on the basis of the zero-point energy effect. An analysis is given of the contributions made by the different types of zero-point vibrations to the total shift.

The shifts observed with the partly deuterated benzenes approximately agree with those which would be deduced by linear interpolation between benzene and hexadeuterobenzene, simply on the basis of the number of deuterium atoms present. This is discussed qualitatively, and is shown to follow plausibly from the known changes which are induced in vibrations by the dissymmetric loading of the molecule.

Correction for the zero-point transition energy leads to a purely electronic transition energy, which is the same for all benzenes.

In this paper we present such conclusions concerning the physics of the states and transitions of the benzene molecule as appear to us to follow from the studies of spectra described in the preceding eleven papers.

(A) *Effect of the* $A_{1g} \rightarrow B_{2u}$ *Electronic Transition on the Geometry and Elastic Properties of the Benzene Molecule.*

(1) *Elastic Constants of the Lower and the Upper States.*—The Wilson–Bell potential-energy function provides a good basis for an assessment of the salient features of the effect of the $A_{1g} \rightarrow B_{2u}$ electronic transition on the elastic properties of the benzene molecule. In Table I we assemble the determined elastic constants, as they have emerged in the calculations reported in Part XI, Section B. The force-constants F and f are in the form already given: they express the restoring forces per unit change of length, r and s, of a C–C bond and of a C–H bond, respectively. However, bending and twisting force-constants are awkward concepts,* and we here replace the formerly used, carbon and hydrogen, planar-bending force-constants, D and d, as well as the out-of-plane carbon-bond twisting and hydrogen-bond bending, force-constants, Q and g, by the corresponding moment-constants, Δ, δ, Γ and γ, respectively. Each of these quantities expresses the restoring moment generated per unit angular deformation. For Δ, the deformation, ρ, is that of an internal ring-angle; for δ, it is the angular deviation, σ, in the plane of the ring, of a C–H bond from the bisector of the external ring-angle; for Γ, it is the angle, Φ, through which a C–C bond is twisted by the out-of-plane displacements of the adjacent atoms; and for γ, it is the angle, μ, by which the bond of a hydrogen atom deviates from the plane of the nearest three carbon atoms. In terms of these constants, the potential energy expression takes the form

$$2V = F\Sigma r^2 + f\Sigma s^2 + \Delta\Sigma\rho^2 + \delta\Sigma\sigma^2 + \Gamma\Sigma\Phi^2 + \gamma\Sigma\mu^2$$

where $\Phi = \phi_C + \phi_H$ (cf. Part XI, Section B, 1), and each sum extends over six like atoms or six like bonds. The relations between the moment-constants and the force-constants are $\Delta = Da^2$, $\delta = db^2$, $\Gamma = Qc^2$, and $\gamma = gb^2$, where a, b, and c are geometrical constants (cf. *loc. cit.*).

TABLE I.

Elastic Constants of the Benzene Molecule in its Normal and Excited States.

	Force-constants (dynes per cm.).		Moment-constants (dyne-cm. per radian).			
	10^{-5} F.	10^{-5} f.	10^{12} Δ.	10^{12} δ.	10^{12} Γ.	10^{12} γ.
Ground state	7·61	5·06	13·7	8·0	1·02	2·62
Excited state	6·53	5·35	10·5	6·6	0·32	1·43
% Drop	14	−6	23	17	68	45

(2) *Stretching Force-constant and Length of the* C–C *Bonds.*—As noted in Part I, Section 2, the electronic excitation $A_{1g} \rightarrow B_{2u}$ involves the promotion of one of the six unsaturation electrons from a molecular orbital of e_g^- symmetry to one of e_u^+ symmetry. On an energy scale, the electron can be considered to have been raised just about half-way towards complete ionisation (ionisation potential, 9·19 electron-volts). From a stereo-electronic standpoint, the excited orbital has one additional nodal surface of indefinite orientation intersecting the geometrical bands, and therefore must have increased anti-bonding properties. From both points of view, one would expect the excitation to diminish both the strength of the C–C bonds and their resistance to stretching.

Consistently with its average content of three electrons, a C–C bond of normal benzene exhibits a degree of resistance to stretching which is intermediate between the degrees of resistance shown by the C–C bonds of normal ethane and ethylene:

Force-constants (F) of the normal molecules	ethane,	benzene,	ethylene.
10^{-5} F (with F in dynes/cm.).....	4·5	7·6	9·8

It is the excess of resistance of the benzene bond, over that shown by the ethane bond, that we should expect to find considerably reduced as a result of the electronic excitation; and thus it seems very reasonable that 10^{-5} F for excited benzene should have a value 6·5, which is well bracketed between 4·5 and 7·6.

Badger's relation between the force-constants and the lengths of bonds (*J. Chem. Physics*,

* The use of the term " bending force-constant " has often led to untidy notations, which its replacement by " moment-constant " would have avoided. Quantities which are really moment-constants have been called " bending force-constants ", and have even been expressed in incorrect units.

1934, **2**, 128) can be made the basis of a procedure for estimating the expansion which the benzene ring undergoes as a result of the electronic excitation. The relation takes the form

$$X = k(x - \kappa_{ij})^{-3}$$

where X is a force-constant in dynes/cm., x is the equilibrium bond-length in Ångström units, k is a universal constant, the best value of which, for general purposes, is $1{\cdot}85 \times 10^5$, and κ_{ij} is a constant which depends on the principal quantum numbers of the bonding electrons, and for a carbon–carbon bond has the value 0·68. If we make the plausible assumption that, for the bond of a benzene ring, the best value of k, though not exactly equal to the general average value, is, to a close approximation, the same for both electronic states, then, using our determined values of F, we can write the following expression for the precentage increase which the carbon bond-length undergoes as a result of the electronic excitation:

$$100(1{\cdot}39 - 0{\cdot}68)\{(7{\cdot}61/6{\cdot}53)^{1/3} - 1\}/1{\cdot}39 = 2{\cdot}7\%$$

Douglas Clark's relationship, $X = Cx^{-6}$ (*Phil. Mag.*, 1934, **18**, 459), gives a similar result. Taking the constant C to be the same in both states, the percentage enlargement becomes

$$100\{(7{\cdot}61/6{\cdot}53)^{1/6} - 1\} = 2{\cdot}6\%$$

Thus the C–C bond-length in the excited molecule is close to 1·43 A.

Kynch and Penney have made a quantum-mechanical calculation, using the electron-pair method, of some of the properties of the excited state of benzene (*Proc. Roy. Soc.*, 1941, *A*, **179**, 266). For the length of the C–C bond they found 1·44 A., in good agreement with the value given above. For the ring-breathing frequency they found 918 cm.$^{-1}$, remarking that "this agrees moderately well with the experimental measurement of 940 cm.$^{-1}$". Of course, it agrees much better with the correct experimental value, 923 cm.$^{-1}$ (cf. Part II, Section 4; the value is 924 cm.$^{-1}$ when correction is applied for the anharmonicity of the vibration).

(3) *Stretching Force-constant and Length of the* C–H *Bonds.*—It might have been expected that the electronic excitation *increases* the vibration frequency and force-constant of the C–H bonds. If we could completely remove one unsaturation electron from a single carbon atom, the effect might well be to shorten the C–H bond considerably, and increase its resistance to stretching, both because of the increased effective nuclear charge of the carbon atom, and because of the incompleteness of its valency shell (Pauling, "Nature of the Chemical Bond", Cornell Press, 1940, p. 169). A rough estimate, based on known bond-lengths, gives 0·1 A. as the probable order of magnitude of the contraction in this case. Actually, the excitation partly removes, from the near locality of each carbon nucleus, one-sixth of an unsaturation electron; and so one may plausibly suppose that the resultant contraction is likely to be only of the order of 0·01 A. This, however, is the correct order of magnitude for correlation with the determined increase of 6% in the force-constant f. Alternatively, we can use known force-constants in order to estimate directly the probable order of magnitude of the increase in force-constant (cf. Herzberg, "Infra-red and Raman Spectra", van Nostrand, 1945, p. 192), and can thus discover that an increase of the order of 5% would be reasonable.

In an application of Badger's relation to a C–H bond, the constant κ_{ij} takes the value 0·34. Using this relation as before, together with the determined values of the force-constant f, we calculate the percentage shortening of the bond thus:

$$100(1{\cdot}08 - 0{\cdot}34)\{1 - (5{\cdot}06/5{\cdot}35)^{1/3}\}/1{\cdot}08 = 1{\cdot}3\%$$

Alternatively, using Douglas Clark's relation as before, we find for the contraction

$$100\{1 - (5{\cdot}06/5{\cdot}35)^{1/6}\} = 0{\cdot}9\%$$

Thus the C–H bond-length in excited benzene lies close to 1·07 A.

Sklar's theory of the electronic transition, and its ample verification in the spectra, establishes the plane-hexagonal (D_{6h}) symmetry of the equilibrium nuclear configuration of the excited benzene molecule. The above estimates of the equilibrium C–C and C–H bond-lengths in the excited state thus complete the determination of the geometry of the model of the excited molecule.

(4) *The Planar Bending Moment-constants.*—Since the planar variations of the three valency angles of any one carbon atom involve the relation that their sum is zero, the individual variations are expressible in terms of two parameters. The constant Δ measures the restoring moment which is produced when the CCC angle changes in one direction by a certain amount, and each CCH angle simultaneously changes in the other direction by half that amount. The

constant δ measures the moment which is called into operation when the two CCH angles simultaneously change in opposite directions by equal amounts, the CCC angle remaining unaltered.

Independently of the unsaturation electrons, the trigonal constitution of the carbon atomic orbitals of the three saturated electron-pair bonds tends to place the latter at angles of 120° to one another; and the repulsive forces of the three electron-pairs on one another tend to keep them close to these relative positions. However, the superposed effect of the unsaturation electrons in helping to maintain the structure is clearly shown by the observed weakening of the restoring moments, as measured by the moment-constants Δ and δ, when the unsaturation shell becomes attenuated as a result of the electronic excitation. We should note that the unsaturation electrons will exert their effect in at least two ways—partly through the repulsive forces which they themselves exert on the different saturated electron-pairs, and partly by shortening the C–C bonds, and thus enabling the three saturated electron-pairs of any one carbon atom to exert stronger repulsive forces on one another than they would otherwise. We cannot say much about the anticipated magnitude of the weakening which will be suffered, as a result of the electronic excitation, by the whole of this contribution of the unsaturation electrons to the angular rigidity of the system; though one might (somewhat naïvely) expect the percentage reduction of the moment-constants Δ and δ to be of the same order of magnitude as that of the stretching force-constant F—in so far as the changes in Δ and δ result from the effects considered. Actually, these should be the only major effects on the constant δ; and we notice (Table I) that the percentage change which it undergoes is, in fact, not very different from that of the force-constant F.

However, the above effects are expected to be reinforced by yet another in the case of the moment-constant Δ. This further effect arises from the repulsive forces between the different spin-coupled electron-pairs of the unsaturation shell itself. These pairs will tend to keep apart, and their repulsion will accordingly tend to open the internal ring-angles. The effect of this will be to steepen, on the side of small angles, the potential hollow which restricts the variation of a ring-angle. But even such a one-sided steepening of the potential hollow must make it narrower, and must therefore increase the angular vibration frequency, and the corresponding moment-constant. The decrease of this contribution to the moment-constant Δ, as the unsaturation shell becomes attenuated by excitation, must also be included amongst the causes of the observed reduction of this constant. We notice (Table I) that the percentage reduction of Δ is, in fact, appreciably larger than is that of the other planar moment-constant δ.

(5) *The Out-of-plane Moment-constants.*—As Table I shows, the two out-of-plane constants, Γ and γ, suffer much more drastic reductions, as a result of the electronic excitation, than do any of the planar elastic constants which we have been considering. This is not difficult to understand.

The constant Γ measures the harmonic resistance of a C–C bond to such torsion as arises from unequal out-of-plane displacements of the atoms attached on each side of it. Now according to our theories of chemical binding, practically the whole of such resistance to torsion must come from the unsaturation electrons; for the saturated electron-pair belonging to any bond is supposed to have full cylindrical symmetry about the line of the bond. It follows that any change in the state of the unsaturation shell must profoundly affect the constant Γ, and that, in particular, a replacement of bonding by antibonding character within the shell, such as occurs during the electronic excitation, must strongly reduce Γ. A second reason for the reduction of Γ consists in the diminution of the non-bonding repulsive forces exerted by the unsaturation shell on the neighbouring saturated electron-pairs.

The second out-of-plane constant, γ, measures the harmonic resistance to the bending of a hydrogen atom out of the plane of the nearest three carbon atoms. Since this type of hydrogen motion is tangential to the contours of electron density of the saturated electron-pairs belonging to the C–C bonds, these electron-pairs will contribute relatively slightly to the harmonic restoring moment. But since the hydrogen motion lies across the common nodal plane of the unsaturation electrons, and is directed as nearly as any bending motion can be towards their density gradients, these electrons will contribute largely to the restoring moment. Thus the harmonic restoring moment will owe its existence largely to the unsaturation electrons.* It should be noted that they exert their effect in this case solely by their repulsive action on the electrons of the C–H bond, and not indirectly through shortening the C–C bond. It follows that any change of state of the unsaturation shell must strongly influence the moment-constant γ; and that, in

* That the saturated electron-pairs can in principle make a finite, if small, contribution to the harmonic restoring moment is not intuitively obvious; but it can be established by an easy calculation.

particular, the attenutation of the shell, as a result of the electronic excitation, must very considerably reduce that constant.

We refer here to the attenuation of the unsaturation shell during excitation, but not to the increase of anti-bonding properties within it, because the latter effect is less important for interactions with outside electron-pairs than when the bonded character of the unsaturation shell itself is in question, as in the problem of the torsion constant Γ. That will be one reason why, although the out-of-plane bending constant γ is, indeed, much reduced, it is not, as Table I shows, so greatly reduced as is the torsion constant Γ.

Finally, a probable relationship between the two hydrogen-bending constants, δ and γ, may be pointed out. As we have seen, the planar-bending moment-constant δ can be considered as made up of two parts, one of which would still be present if the unsaturation shell could be removed, whilst the other is due to the unsaturation shell. Only the latter part is strongly reduced by the electronic excitation. It follows that we may take the observed value of $\delta_{ground} - \delta_{excited}$ as a lower limit to the value, in the electronic ground state, of that part of δ which depends on the unsaturation electrons. Now if the ground-state value of this part of δ were entirely determined by the repulsion between the unsaturation electrons and the electrons of the C–H bond, we could at once assert that it must be smaller than the ground-state value of γ, which is mainly determined by the type of electron repulsion specified. This follows because, in the planar motion, the denser parts of the electron cloud of the C–H bond move in the near neighbourhood of, and parallel to, the common nodal plane of the unsaturation electrons, and quite obliquely to their density gradients; whereas, on the contrary, the out-of-plane motion is directed across the nodal plane, and much more nearly towards the density gradients. The conclusion would thus be that a quantity which is substantially larger than $\delta_{ground} - \delta_{excited}$ is also substantially smaller than γ_{ground}. But we have noted before that the part of δ which depends on the unsaturation electrons, although it arises largely through the mechanism of direct repulsion between these electrons and the electrons of the C–H bond, must also to some extent be due to an indirect effect arising through the shortening influence of the unsaturation electrons on the C–C bonds. Our conclusion must therefore be modified to the following, *viz.*, that a quantity which is somewhat smaller than that mentioned above, and which, therefore, may not be very different from $\delta_{ground} - \delta_{excited}$, must be substantially smaller than γ_{ground}. That is to say, the quantity $\delta_{ground} - \delta_{excited}$ itself is likely to be definitely smaller than γ_{ground}. This expected relationship is fulfilled by the data of Table I.

(6) *Note on the Assignments of Planar Hydrogen-bending Frequencies to the Excited State.*—In so far as our assignments of upper-state frequencies to the planar hydrogen-bending vibrations of benzene in its different isotopic forms rest on evidence of a direct spectral nature, they are less well supported than are the spectrally-based assignments to vibrations of other types. However, the preceding argument provides some general confirmation of the assignments we have adopted. For essentially it is these assignments which determine the moment-constant $\delta_{excited}$. The above conclusion, that $\delta_{excited}$ should fall below δ_{ground} by an amount which is substantially less than γ_{ground}, means that $10^{12}\,\delta_{excited}$ should fall well within the range $6{\cdot}7 \pm 1{\cdot}3$. Since frequencies shift comparably to the square-roots of moment-constants, this in turn means that the planar hydrogen-bending frequencies should not lie many units per cent. away from the values we have assigned to them. A further argument pointing to the same conclusion is mentioned later (Section B, 5).

(B) *Effect of the* A_{1g}—B_{2u} *Electronic Excitation on the Zero-point Energy of the Benzene Molecule; and the Effect of Isotopic Substitution on the Energy of the* A_{1g}—B_{2u} *Electronic Transition.*

(1) *The Isotopic Shift of the Electronic Origin.*—Since the transition A_{1g}—B_{2u} is forbidden, no 0—0 band appears to mark the position of the electronic origin of the band-system, and thus to give directly the energy of the electronic transition. However, Sklar's identification of the upper electronic state, and Nordheim, Sponer, Sklar, and Teller's explanation of the mechanism through which the transition becomes observable, are so well proven that the position of the origin in the spectrum of any of the isotopically isomeric benzenes which have been studied can be fixed with as much certainty as if it were marked by a visible band. In Parts II—X the positions of the origins of the various band-systems are given. These figures are now assembled in Table II. It is unlikely that any of the figures is in error by more than 2 cm.$^{-1}$.

One notices that the different isotopically isomeric benzenes have not all the same electronic origin: that of hexadeuterobenzene lies 200 cm.$^{-1}$ further out towards the far-ultraviolet than that of benzene. Furthermore, the shift with isotopic substitution is an approximately linear function of the number of deuterium atoms present in the molecule. A finer point is that

the departures from linearity appear to be systematic, in the sense that the origin frequencies of the middle members of the series, those with two, three, and four deuterium atoms, lean slightly towards lower values than the linearly interpolated ones, the deviation being greatest for the central member, 1 : 3 : 5-trideuterobenzene.

TABLE II.

Frequencies (cm.$^{-1}$) of the Electronic Origins of the First Ultraviolet Band-systems of the Isotopically Isomeric Benzenes, as observed in either Fluorescence or Absorption.

	Origin frequency.	Difference.	Deviation from linearity.
Benzene	38090		± 0
		34	
Monodeuterobenzene	38124		+ 1
		30	
1 : 4-Dideuterobenzene	38154		− 3
		30	
1 : 3 : 5-Trideuterobenzene	38184		− 6
		35	
1 : 2 : 4 : 5-Tetradeuterobenzene	38219		− 4
Pentadeuterobenzene	—	2 × 35	—
Hexadeuterobenzene	38290		± 0

(2) *The Contribution of Vibrational Zero-point Energy to the Transition Energy.*—We shall show that practically the whole of the observed shift is due to vibrational zero-point energy. The energy of an electronic transition is not simply the difference between the electronic energies of the two combining states : it is this, *plus* the difference between their nuclear-zero-point energies. To a very close approximation the electronic energy of each state remains the same in an isotopic substitution, and therefore the difference between the electronic energies of the two states remains the same. However, the vibrational zero-point energy of each state will be changed by isotopic substitution, and, if the changes are different, then the contribution of the zero-point energy to the transition energy will be different for the isotopically isomeric molecules.

For simplicity, let us consider a vibration of benzene which is alone in its symmetry class, *e.g.*, the vibration E_g^-(H). We can then discuss it independently of the other vibrations. Since it is doubly degenerate, its contribution to the zero-point energy ($h\nu/2$ in each of two degrees of freedom), if expressed in frequency units, is equal to its fundamental frequency. For the electronic ground state, this is 849 cm.$^{-1}$. In the electronic excitation the forces are loosened and the frequency drops, so that the contribution of this vibration to the zero-point energy of the upper electronic state is only 585 cm.$^{-1}$. The difference between these two quantities, −264 cm.$^{-1}$, is the contribution of the zero-point energy of the vibration to the energy of a transition from one " vibrationless " electronic state to the other. Its sign is opposite to that of the electronic energy difference, so that its effect is to shift the electronic origin to a lower frequency than that which the origin would have if there were no zero-point energy. Starting again in the ground state, we make the isotopic substitution which converts benzene into hexadeuterobenzene, thus reducing the fundamental frequency, and therefore the zero-point energy contribution, of the vibration by a factor which is given by the product rule. This energy is, in fact, reduced to 662 cm.$^{-1}$. In the upper electronic state also, the zero-point energy contribution becomes reduced by a factor, which is likewise given by the product rule, and is very nearly the same as before. This energy accordingly becomes 454 cm.$^{-1}$. The difference between these two quantities, −208 cm.$^{-1}$, could obviously be calculated by reducing the former difference, −264 cm.$^{-1}$, by almost the same factor. (The various factors can be considered identical, if we agree to neglect anharmonicity and the small difference in the size of the molecule in its two electronic states.) Each of the differences, −264 cm.$^{-1}$ for benzene, and −208 cm.$^{-1}$ for hexadeuterobenzene, is a negative contribution to the energy of electronic excitation of the relevant molecule : each shifts the origin towards lower frequencies, but the reduction of frequency is greater for benzene than for hexadeuterobenzene. Thus the difference between the differences, + 56 cm.$^{-1}$, represents the contribution of the zero-point energy of this vibration to the upward displacement of the excitation energy of hexadeuterobenzene relatively to that of benzene.

Only three vibrations of benzene are alone in their symmetry classes, and it is not theoretically rigorous to discuss the other seventeen on similar lines. But to quite a reasonable degree of approximation one may do so. For it has been shown empirically that the electronic excitation not only reduces, as the product theorem necessitates, the products of frequencies of the same symmetry class by substantially the same factor for benzene and hexadeuterobenzene : it also reduces each individual frequency by approximately the same factor for both compounds (cf. Part XI, Section B, 3, especially Table IV). This fact is sufficient to ensure that any

vibration whose frequency is considerably reduced by the conversion of benzene into hexadeuterobenzene, and is also considerably reduced by the electronic excitation, will act like the E_2^-(H) vibration considered above: it will supply to the energy of the electronic excitation of each compound a contribution, consisting of a difference of zero-point energies, which displaces the electronic origin towards lower frequencies, but does so in such a way as to leave the electronic origin of hexadeuterobenzene at a higher frequency than that of benzene.

The great majority of the vibrations of benzene have their frequencies reduced both by complete deuteration of the molecule and by the electronic excitation, although in some cases the changes are not very large. All these, if they have any decided effect on the relative positions of the electronic origins, will act in the way described. Thus it is not unnatural that the total contribution of the zero-point energy of all the vibrations to the energy of the electronic excitation should be of the kind illustrated; and that, accordingly, we should, as we do, find that the electronic origin of the hexadeuterobenzene transition lies at a higher frequency than that of the benzene transition.

One group of vibrations is anomalous, *viz.*, the hydrogen-stretching vibrations. These have their frequencies reduced (obviously) by deuteration, but increased quite appreciably by the electronic excitation. It will be evident from the foregoing discussion that the zero-point energy contribution of such vibrations will be in the direction of raising the energy of the electronic excitation; and furthermore, that the magnitude of the contribution will be greater for benzene than for hexadeuterobenzene. It follows that, if this difference were the dominating one, the electronic origin of the transition of benzene would lie higher than that of the transition of hexadeuterobenzene. However, the effect of the hydrogen-stretching vibrations is, in fact, not powerful enough to prevail against the contrary action of all the other vibrations.

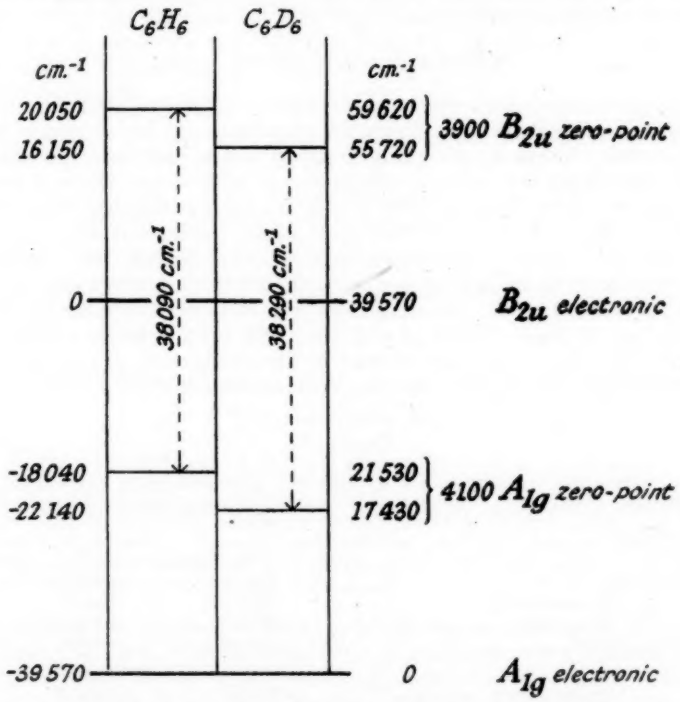
We now turn to the partly deuterated benzenes. One might have expected that their electronic origins would space themselves out according to the number of deuterium atoms; and that, in rough approximation, the spacing would correspond to a linear interpolation between the electronic origins of benzene and hexadeuterobenzene. It is true that, as symmetry is reduced by the isotopic loading of the partly deuterated benzenes, with the consequence that certain vibrational symmetry classes become fused together, many of the vibrations which are characteristic of benzene and hexadeuterobenzene become mixed. But when two vibrations thus mix, even when they do so rather completely, as do, *e.g.*, the ring-swelling, and plane-trigonal ring-bending, vibrations of benzene or hexadeuterobenzene in forming the two totally symmetrical carbon vibrations of 1 : 3 : 5-trideuterobenzene (cf. *J.*, 1946, 259, 260), the effect on the frequencies is merely to push them apart in such a way that their sum, and therefore the sum of their zero-point energies, is not very different from what it would have been if the isotopic loading of the molecule had been so levelled out as to stop the mixing, *i.e.*, if, in this example, the molecule had been supplied with six hydrogen atoms of atomic weight 1·5. In short, the sum of the frequencies will not differ greatly from a linearly interpolated sum. Many of the mixings which occur when successive deuterium atoms are introduced into benzene are more complicated than this, and, in particular, involve more than two vibrations; but such mixings may be analysed into successive two-component mixings, and thus the rough principle of a linear shift of summed frequencies may be expected still to hold. Furthermore, the deviations shown by particular groups of mixed vibrations, due to the dissymmetric pushing apart of frequencies, are likely to occur about equally often in either direction, so that for the complete sum of all the vibration frequencies, and therefore for the total vibrational zero-point energy, the law of linear interpolation might be expected to hold rather well. Now all this is true not only for the ground state, but also for the excited state. Therefore linear interpolation should hold, not only for each state separately, but also for the difference between the zero-point energies of the ground and the excited states. In short, it should hold for the contribution of zero-point energy to the energy of excitation, and for the effect of zero-point energy on the position of the electronic origin.

We can offer no correspondingly simple treatment of the small, but apparently systematic, deviations from the linear relationship which the observational figures disclose, because the errors introduced by the simplifications tried cannot be shown to be of a smaller order of magnitude than that of the deviations themselves.

(3) *The Isotope Effect on the Electronic Part of the Transition Energy.*—The second conceivable cause of isotope shifts in the electronic origins of the band systems is the occurrence in the molecular case of the effect, with which we are familiar in atoms, arising from the altered reduced masses of the electrons. Although we cannot calculate this effect in molecules, it is easy to show that it must be too small to have any relevance to the present observations.

The Rydberg constants for a protium atom and a deuterium atom differ as 1 differs from $1 + 1/(2 \times 1835)$. Therefore, if the benzene transition, amounting as it does to 38090 cm.$^{-1}$, consisted in the excitation of an electron which belonged entirely to one hydrogen atom, or entirely to all the hydrogen atoms, and not to any of the carbon atoms, we should expect the electronic energy of the transition to be altered in hexadeuterobenzene, on account of the altered reduced mass of the electron, by a quantity of the order of $38090/3670 = 10$ cm.$^{-1}$. But we believe that the optical electron has actually very little to do with the hydrogen atoms, and that it belongs essentially to the carbon atoms. For this reason we do not expect the isotope shift in the purely electronic part of the excitation energy to be of a greater order of magnitude than 1 cm.$^{-1}$—which is the order of the experimental error.

(4) *Quantitative Comparisons for Benzene and Hexadeuterobenzene.*—From the last paragraph it follows that, in seeking to establish a quantitative connexion between theory and experiment,



Electronic and zero-point energy levels (cm.$^{-1}$) of the A_{1g} and B_{2u} states of benzene and hexadeuterobenzene.

we can confine attention to the isotope shift in the zero-point energy contribution to the transition energy. A quantitative test is possible for benzene and hexadeuterobenzene, because for these molecules we have complete sets of vibration frequencies, not only for the electronic ground state (Herzfeld, Ingold, and Poole, *J.*, 1946, 332), but also for the upper electronic state (Part XI, Tables V and VI, this vol., pp. 506, 507). The cases of the partly deuterated benzenes can then be allowed to rest on the discussed rule of linear interpolation.

The results of the test, applied to benzene and hexadeuterobenzene, are shown in Table III; in which, for convenience, we express energies in wave-numbers. The calculated isotopic shift of the electronic origin is 208 cm.$^{-1}$, whilst the observed shift is 200 cm.$^{-1}$. The agreement is closer than one had any right to expect, having regard to the errors to which the frequencies are liable.

Attention may be directed to the considerable magnitude of the zero-point energy of benzene. It appears that one would have to heat that substance to more than 1300° c. in order to add as much energy again, or to more than 1500° c. to add as much vibrational energy, as the molecule already possesses at the absolute zero of temperature. A remarkable fact is that the zero-point energy in either state is of the order of one-half of the energy of the electronic transition. This is shown in the figure, which is a graphical expression of the data for benzene and hexadeutero-

TABLE III.

Zero-point Energies (cm.$^{-1}$) of the States and Transitions of Benzene and Hexadeuterobenzene, interpreting the Isotope Shift of the Electronic Origin of their Band Systems.

	C_6H_6.	C_6D_6.	Isotope shift.
Excited state (B_{2u})	20050	16154	− 3896
Ground state (A_{1g})	21535	17431	− 4104
Transition (A_{1g}—B_{2u})	− 1485	− 1277	+ 208

benzene, contained in Tables II and III, the units of wave-numbers having been rounded off in order to secure consistency. The figure shows that the electronic transitions actually take place rather far from those positions in the energy diagram in which we usually think of them.

The change of purely electronic energy associated with the A_{1g}—B_{2u} transition of either benzene or hexadeuterobenzene is

$$39570 \text{ cm.}^{-1} = 4{\cdot}88 \text{ electron-volts.}$$

It is of interest to examine how the various types of vibrations contribute to the shift of the electronic origin. For this purpose we divide the vibrations into four groups. The first consists of all the planar carbon vibrations, stretching, bending, and deformation, the frequencies of which are not greatly altered by the isotopic substitution. The second is the group of hydrogen-stretching vibrations. The third consists of the planar hydrogen-bending vibrations. The fourth comprises all the out-of-plane vibrations, in most of which hydrogen and carbon types of motion are not at all sharply separated from one another (cf. *J.*, 1946, 261, *et seq.*). An analysis of the effects attributable to these four sets of vibrations is set out in Table IV. One sees that the carbon vibrations have very little effect on the isotopic displacement of the transition energy; that the out-of-plane vibrations could account for the whole of the observed effect; but that the hydrogen-stretching and planar hydrogen-bending groups of vibrations make significant contributions, which, however, largely cancel each other.

TABLE IV.

Analysis of the Contributions made by Four Groups of Vibrations to the Zero-point Energies (cm.$^{-1}$) of the States and Transitions of Benzene and Hexadeuterobenzene, and to the Shift of the Electronic Origin.

		C_6H_6.	C_6D_6.	Isotope shift.
Excited state	Planar C	5170·0	4851·5	318·5
	,, H-stretching	9340·0	6960·0	2380·0
	,, H-bending	3180·0	2415·0	765·0
	Out-of-plane	2360·5	1927·5	433·0
Ground state	Planar C	5511·4	5200·5	310·9
	,, H-stretching	9187·7	6850·3	2337·4
	,, H-bending	3433·0	2611·3	821·7
	Out-of-plane	3403·4	2768·9	634·5
Transition	Planar C	− 341·4	− 349·0	− 7·6
	,, H-stretching	+ 152·3	+ 109·7	− 42·6
	,, H-bending	− 253·0	− 196·3	+ 56·7
	Out-of-plane	− 1042·9	− 841·4	+ 201·5
Transition (total)		− 1485·0	− 1277·0	+ 208·0

The reason why the nine carbon vibrational degrees of freedom make no significant contribution to the displacement of the origin is because this appears as a second difference, and the carbon frequencies, although they are appreciably reduced by the electronic excitation, are not greatly shifted by the isotopic substitution. All the other groups of frequencies are considerably shifted by the isotopic substitution; but the reason why the out-of-plane vibrations, with their nine degrees of freedom, exert so very much more influence on the displacement of the origin than do either of the planar hydrogen groups, each with six degrees of freedom, is that the out-of-plane vibrations suffer a much larger diminution of frequency as a result of the electronic excitation than do the planar vibrations. The contrary signs of the moderate contributions made by the hydrogen-stretching and planar hydrogen-bending groups of vibration are evidently to be correlated with the circumstance that the stretching frequencies are increased, whilst the bending frequencies are decreased, by the excitation.

(5) *Further Note on the Upper-state Assignments of Planar Hydrogen-bending Frequencies.*—The preceding analysis provides some further confirmation of the conclusion (cf. Section A, 6) that our assignments of planar hydrogen-bending frequencies, in the upper electronic states of the various isotopically isomeric benzenes, are substantially correct; and all such confirmation is welcome, because the direct spectral evidence on which that particular series of assignments originally rested was somewhat slender. The present argument is as follows. Since the zero-point energy of the out-of-plane vibrations, the frequencies of which are well supported, could by itself account for the whole of the observed shift of the electronic origin, and since the planar carbon vibrations can make very little contribution to the shift, it is evident that the contributions of the planar hydrogen-stretching and hydrogen-bending vibrations have got, roughly, to balance. Isotopic substitution reduces the hydrogen-stretching and hydrogen-bending frequencies by similar factors. Electronic excitation increases the hydrogen-stretching frequencies, and the order of magnitude of the increase is well-documented. It follows that the electronic excitation must decrease the hydrogen-bending frequencies by an average amount, that can be roughly computed from the condition that it must produce the balancing described. This computed average decrease is in fairly good agreement with our assignments of the hydrogen-bending frequencies.

The authors of this group of papers wish to thank the University of London for a Scholarship, and the Department of Scientific and Industrial Research for a stipend, granted to one of their number; and also to thank Imperial Chemical Industries Ltd. for their gift of the heavy water which was employed to produce the deuterated benzenes used in this work. Mr. A. Maccoll and Dr. D. P. Craig gave the authors some valuable criticisms of the present paper, enabling its text to be improved in several places.

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107. *Synthesis of Alloxazine from 2-Aminoquinoxaline-3-carboxyamide.*

By A. H. GOWENLOCK, G. T. NEWBOLD, and F. S. SPRING.

The conversion of 2-aminoquinoxaline-3-carboxylic acid (and its derivatives) into alloxazine, although more difficult than the analogous conversion of anthranilic acid into dihydroxyquinazoline, has been achieved. Treatment of 2-aminoquinoxaline-3-carboxyamide with ethyl chloroformate gives 2-carbethoxyaminoquinoxaline-3-carboxyamide which on treatment with sodium ethoxide yields alloxazine in high yield.

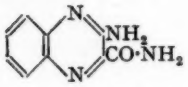
ALLOXAZINE derivatives are usually prepared by the condensation of an *o*-diamine with alloxan (Kuhling, *Ber.*, 1891, **24**, 2363; Mohlau and Litter, *J. pr. Chem.*, 1906, **73**, 481); a second type of synthesis consists in the condensation of an *o*-quinone with 5 : 6-diamino-2 : 4-dihydroxypyrimidine (Kuhn and Cook, *Ber.*, 1937, **70**, 761), although the method fails in the case of *o*-benzoquinone. Both methods require a preformed pyrimidine ring, and in each a pyrazine ring is formed by the condensation reaction. A third method in which quinoxaline-2 : 3-dicarboxyamide is converted into alloxazine (Baxter and Spring, *J.*, 1945, 229) differs from the first two in that it requires a preformed pyrazine ring, the reaction resulting in the formation of the pyrimidine ring. The last method is comparable with the preparation of 2 : 4-dihydroxyquinazoline from phthalamide (Hoogewerff and van Dorp, *Rec. Trav. chim.*, 1891, **10**, 4; 1896, **15**, 107). This paper describes attempts to synthesise alloxazine and other pyrimidoquinoxaline derivatives by adaptations of methods for the synthesis of substituted quinazolines from benzene derivatives.

Anthranilic acid and anthranilamide have been converted into 2 : 4-dihydroxyquinazoline by heating with urea (Abt, *J. pr. Chem.*, 1889, **39**, 140). Similar treatment of 2-aminoquinoxaline-3-carboxylic acid and 2-aminoquinoxaline-3-carboxyamide gave complex mixtures, and, although there was some evidence of the formation of alloxazine, satisfactory conditions for using these routes to alloxazine were not developed. Equally unsuccessful was an attempt to condense 2-aminoquinoxaline-3-carboxylic acid with cyanogen in alcoholic solution using conditions which lead to the formation of 4-hydroxy-2-ethoxyquinazoline from anthranilic acid (Griess, *Ber.*, 1869, **2**, 416; 1878, **11**, 1987).

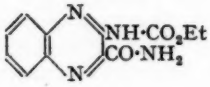
A method for the conversion of the readily available 2-aminoquinoxaline-3-carboxyamide (I) (Gowenlock, Newbold, and Spring, *J.*, 1945, 622) into alloxazine was developed by condensation

of the amino-amide with ethyl chloroformate to give 2-*carbethoxyaminoquinoxaline*-3-*carboxyamide* (II) in 70% yield. When treated with ethanolic sodium ethoxide, (II) gave alloxazine (III) in 80% yield.

Treatment of 2-aminoquinoxaline-3-carboxyamide (I) with acetic anhydride gives 6-*hydroxy*-2-*methylbenzopteridine* (IV). A second product of this reaction is a *monoacetyl* derivative, $C_{13}H_{10}O_2N_4$, m. p. 104—105°, hydrolysis of which yields (IV). Acetylation of (IV) yields the same monoacetyl derivative. The relatively low melting point of the monoacetyl derivative suggests that it is 6-acetoxy-2-methylbenzopteridine rather than the isomeric *N*-acetyl compound.



(I.)



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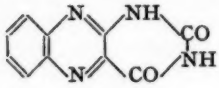

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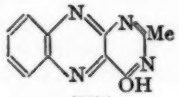

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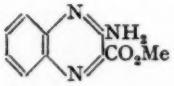

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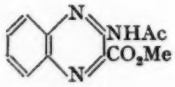

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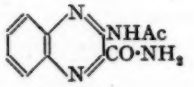

(VII.)

Acetylation of methyl 2-aminoquinoxaline-3-carboxylate (V) (Gowenlock, Newbold, and Spring, *loc. cit.*) gives *methyl* 2-*acetamidoquinoxaline*-3-*carboxylate* (VI) in high yield. Treatment of (VI) with ammonia yields 2-*acetamidoquinoxaline*-3-*carboxyamide* (VII) which when heated with acetic anhydride gives the monoacetyl derivative of 6-hydroxy-2-methylbenzopteridine (IV). Attempts to cyclise 2-acetamidoquinoxaline-3-carboxyamide (VII) by simple solution in alkali, a procedure which leads to the formation of 4-hydroxy-2-methylquinoxaline from the analogously constituted 2-acetamidobenzamide, were unsuccessful.

Experimental.

2-Carbethoxyaminoquinoxaline-3-carboxyamide (II).—2-Aminoquinoxaline-3-carboxyamide (Gowenlock, Newbold, and Spring, *loc. cit.*) (1 g.) and ethyl chloroformate (25 c.c.) were refluxed for 20 hours; hydrogen chloride was continuously evolved. The excess of ester was removed under reduced pressure and the residue crystallised from methanol to give 2-*carbethoxyaminoquinoxaline*-3-*carboxyamide* as pale yellow needles (yield, 70%). It is readily soluble in chloroform and glacial acetic acid at room temperature and in hot alcohol, benzene, acetone, and ethyl acetate; it decomposes above 300° (Found: C, 55·5; H, 4·4; N, 21·8. $C_{12}H_{12}O_3N_4$ requires C, 55·4; H, 4·6; N, 21·5%).

Alloxazine.—(*a*) 2-Carbethoxyaminoquinoxaline-3-carboxyamide (0·8 g.) was refluxed with a solution of potassium hydroxide (3·2 g.) in 60% alcohol (60 c.c.) for 3 hours. The hot solution was acidified (Congo-red) with hydrochloric acid and the yellow precipitate (0·43 g.) collected. The filtrate was evaporated to dryness under reduced pressure and the residue extracted with hot glacial acetic acid. When the extract was cooled, 2-aminoquinoxaline-3-carboxylic acid separated as yellow needles, m. p. 212° (decomp.) undepressed in m. p. when mixed with an authentic specimen prepared as described by Baxter and Spring (*loc. cit.*). The yellow precipitate was purified by dissolution in hot 2% sodium hydroxide; after filtration and cooling, the solution deposited the sodium salt of alloxazine as yellow needles. The sodium salt was dissolved in aqueous alcohol and the solution acidified with acetic acid, alloxazine separating as a pale yellow powder decomposing without melting above 300°. Light absorption in ethanol: Maxima at 3220 A. ($\varepsilon = 5900$) and 2460 A. ($\varepsilon = 19{,}000$). It was characterised by conversion into 1 : 3-dimethylalloxazine which separated from alcohol as bright yellow prisms, m. p. 234—236°, undepressed when mixed with an authentic specimen (Found: C, 59·2; H, 3·9; N, 23·2. Calc. for $C_{12}H_{10}O_2N_4$: C, 59·5; H, 4·1; N, 23·2%). Light absorption in ethanol: maxima at 2450 A. ($\varepsilon = 38{,}200$), 3245 A. ($\varepsilon = 6900$), and 3780 A. ($\varepsilon = 7200$).

(*b*) 2-Carbethoxyaminoquinoxaline-3-carboxyamide (450 mg.) was heated under reflux with a solution of sodium ethoxide in ethanol (from 70 c.c. of alcohol and 450 mg. of sodium). The amide quickly dissolved and the resulting yellow solution slowly deposited a bright yellow solid. The solvent was removed (reduced pressure) and the residual solid dissolved in hot 2% sodium hydroxide (25 c.c.). The hot solution was filtered, and on cooling deposited the sodium salt of alloxazine as yellow needles treatment of which as described above gave alloxazine (330 mg.) as a pale yellow powder decomposing without melting above 300°, characterised by conversion into 1 : 3-dimethylalloxazine which separated from methyl alcohol as yellow prisms, m. p. 238—240° undepressed when mixed with an authentic specimen.

Methyl 2-Acetamidoquinoxaline-3-carboxylate.—A solution of methyl 2-aminoquinoxaline-3-carboxylate (0·5 g.) in acetic anhydride (3 c.c.) was heated under reflux for 1 hour. The solution was evaporated under reduced pressure and the residue crystallised from benzene–light petroleum (b. p. 40—60°) to give *methyl* 2-*acetamidoquinoxaline*-3-*carboxylate* (0·41 g.) as needles, m. p. 143—144° (Found: C, 59·1; H, 4·3; N, 16·9. $C_{13}H_{11}O_3N_3$ requires C, 58·8; H, 4·5; N, 17·1%).

2-*Acetamidoquinoxaline*-3-*carboxyamide.*—A solution of methyl 2-acetamidoquinoxaline-3-carboxylate (0·48 g.) in methanol (25 c.c.) was saturated with dry ammonia at 0° and kept at this temperature for

1 hour. The crystalline deposit was collected and recrystallised from aqueous methanol; *2-acetamidoquinoxaline-3-carboxyamide* (0·39 g.) was thus obtained as fine needles, m. p. 207° (decomp.) (Found: C, 57·4; H, 4·2; N, 24·2: $C_{11}H_{10}O_2N_4$ requires: C, 57·4; H, 4·3; N, 24·3%).

6-Hydroxy-2-methylbenzopteridine—(*a*) 2-Aminoquinoxaline-3-carboxyamide (2 g.) was refluxed with acetic anhydride (15 c.c.) for ¾ hour. The solution was evaporated under reduced pressure and the residue extracted with hot methanol. Fractional crystallisation of the extracted material from aqueous methanol gave a less soluble fraction which separated as fine needles; these after recrystallisation from the same solvent or from *n*-hexane gave the *monoacetyl* derivative of 6-hydroxy-2-methylbenzopteridine (0·57 g.) as needles, m. p. 104—105° (Found: C, 61·2; H, 4·2; N, 22·5. $C_{13}H_{10}O_3N_4$ requires C, 61·4; H, 3·9; N, 22·0%). Light absorption in ethanol: maxima at 2480 A. ($\varepsilon = 2930$) and 3295 A. ($\varepsilon = 6000$).

The mother liquors obtained after the isolation of the monoacetyl derivative gave a second crop of crystalline solid on standing. Recrystallisation of this yielded *6-hydroxy-2-methylbenzopteridine* (0·32 g.) which after several recrystallisations from aqueous methanol separated as felted needles, m. p. 185—187°. It is moderately soluble in hot water, from which it can be crystallised, and readily soluble in methanol, ethanol, and acetic acid. It is soluble in cold N-sodium hydroxide and precipitated from the alkaline solution by acidification with N-hydrochloric acid (Found: C, 62·0; H, 4·1. $C_{11}H_8ON_4$ requires C, 62·3; H, 3·8%). Light absorption in ethanol: maxima at 2440 A. ($\varepsilon = 28{,}300$) and 3420 A. ($\varepsilon = 5{,}800$).

The monoacetyl derivative (50 mg.) was warmed with 0·5N-sodium hydroxide (1·8 c.c.) until solution was complete. The bright yellow solution was treated with N-hydrochloric acid (0·9 c.c.) and the precipitated solid collected and crystallised from aqueous methanol; 6-hydroxy-2-methylbenzopteridine was thus obtained as needles, m. p. 185—187° undepressed when mixed with the specimen described above.

6-Hydroxy-2-methylbenzopteridine (70 mg.) was refluxed with acetic anhydride (2 c.c.) for ¾ hour. The solution was evaporated under reduced pressure and the residue crystallised from aqueous methanol to give the monoacetyl derivative as fine needles, m. p. 103—104° not depressed when mixed with the specimen described above.

(*b*) A solution of 2-acetamidoquinoxaline-3-carboxyamide (0·5 g.) in acetic anhydride (7·5 c.c.) was heated under reflux for 3 hours. The solvent was removed under reduced pressure and the residual solid extracted with boiling *n*-hexane (2 × 10 c.c.). Removal of the solvent from the extract followed by crystallisation from aqueous methanol gave the acetyl derivative of 6-hydroxy-2-methylbenzopteridine as fine needles, m. p. 104—105° not depressed on admixture with the specimen described above.

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[*Received, May 1st*, 1947.]

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108. *The Oxidation of 2-Hydroxyquinoxaline and its Derivatives with Hydrogen Peroxide.*

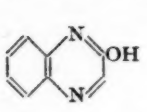
By G. T. NEWBOLD and F. S. SPRING.

Hydrogen peroxide oxidation of 2-hydroxyquinoxaline, 2-hydroxyquinoxaline-3-carboxylic acid, and quinoxaline-2 : 3-dicarboxylic acid gives 2 : 3-dihydroxyquinoxaline in each case. Similar oxidation of 2-ethoxyquinoxaline gives 3-ethoxyquinoxaline 1-oxide (XI) which on treatment with mineral acid yields 2 : 3-dihydroxyquinoxaline. Similarly, 2-ethoxy-3-methylquinoxaline is converted into 3-ethoxy-2-methylquinoxaline 1-oxide (XVII) which on treatment with hydrochloric acid gives 2-hydroxy-3-chloromethylquinoxaline (XVIII).

IN connection with a study of the antibacterial compound aspergillic acid, which has been formulated as a cyclic hydroxamic acid related to pyrazine, model experiments were undertaken with the object of developing a synthesis of acids of this type. Since various methods are now available for the synthesis of hydroxypyrazines (see Baxter, Newbold, and Spring, *J.*, 1947, 370, where the earlier literature is reviewed), a method for the direct oxidation of a hydroxypyrazine to a pyrazinehydroxamic acid would be most attractive; because of their greater accessibility, 2-hydroxyquinoxaline derivatives rather than 2-hydroxypyrazine derivatives were chosen for preliminary examination. This paper describes the behaviour of various 2-hydroxyquinoxaline derivatives when oxidised with hydrogen peroxide.

Oxidation of quinoxaline with hydrogen peroxide gives quinoxaline di-*N*-oxide (McIlwain, *J.*, 1943, 322). Similar oxidation of 2-hydroxyquinoxaline (I) (Gowenlock, Newbold, and Spring, *J.*, 1945, 622) gives 2 : 3-dihydroxyquinoxaline (II), characterised by methylation with methyl sulphate and sodium hydroxide to 2 : 3-*diketo*-1 : 4-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline* (III), m. p. 256—258°. That *N*-methylation had occurred in this reaction was indicated by the high melting point of the product and was established by the preparation of the isomeric 2 : 3-dimethoxyquinoxaline (IV), m. p. 92—94°, by the action of sodium methoxide on 2 : 3-dichloroquinoxaline (V) (cf. Stevens, Pfister, and Wolf, *J. Amer. Chem. Soc.*,

1946, **68**, 1038). 2 : 3-Dihydroxyquinoxaline (which does not melt below 360°) was further characterised by its absorption spectrum in alkaline solution. The susceptibility to oxidation at the 3-position in 2-hydroxyquinoxaline derivatives was further demonstrated in attempts to obtain *N*-oxides from 2-hydroxyquinoxaline-3-carboxylic acid (VI) and quinoxaline-2 : 3-dicarboxylic acid (VII) by oxidation with hydrogen peroxide; in each case 2 : 3-dihydroxyquinoxaline was obtained as sole product. These reactions bear a formal relationship to the formation of acetic acid by the oxidation of pyruvic acid with hydrogen peroxide, the electron-attracting nuclear $-\overset{|}{C}=N-$ grouping in the quinoxaline derivatives functioning as the carbonyl group in pyruvic acid.



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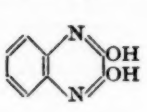

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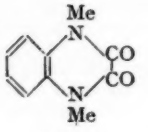

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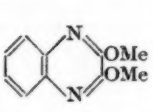

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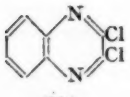

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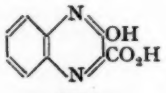

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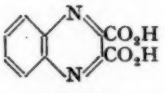
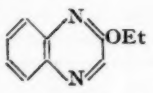


(VII.)

Oxidation of 2-ethoxyquinoxaline (VIII) (Gowenlock, Newbold, and Spring, *loc. cit.*) with hydrogen peroxide yields a compound, $C_{10}H_{10}O_2N_2$, which on hydrolysis with mineral acid yields 2 : 3-dihydroxyquinoxaline, a behaviour which appears to indicate that it is 2-hydroxy-3-ethoxyquinoxaline (IX). The latter compound was synthesised by the following route. Treatment of 2 : 3-dichloroquinoxaline (V) with one mol. of sodium ethoxide gave *2-chloro-3-ethoxyquinoxaline* (X) which, when treated with potassium hydroxide, yielded *2-hydroxy-3-ethoxyquinoxaline*, which proved to be different from the compound obtained by oxidation of 2-ethoxyquinoxaline. Unlike 2-hydroxy-3-ethoxyquinoxaline, the compound $C_{10}H_{10}O_2N_2$ is insoluble in alkali; the oxygen atom introduced into 2-ethoxyquinoxaline by peroxide oxidation cannot be present as a hydroxyl group and is, therefore, probably present as a *N*-oxide group, a decision confirmed by the observation that the compound $C_{10}H_{10}O_2N_2$ liberates iodine from potassium iodide solution in the presence of acetic acid by a procedure which also gives a positive reaction with quinoxaline di-*N*-oxide (McIlwain, *loc. cit.*). The compound $C_{10}H_{10}O_2N_2$ is therefore either *3-ethoxyquinoxaline 1-oxide* (XI) or 2-ethoxyquinoxaline 1-oxide (XII). The fact that acid hydrolysis of the compound gave 2 : 3-dihydroxyquinoxaline and not a cyclic hydroxamic acid, together with the observation that 2 : 3-diethoxyquinoxaline is not oxidised by hydrogen peroxide, established the structure (XI). The rearrangement of an aromatic *N*-oxide to a cyclic amide by treatment with mineral acid does not appear to have been observed previously; quinoxaline di-*N*-oxide is recovered unchanged after refluxing with mineral acid under the same conditions.



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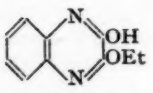

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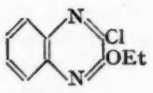

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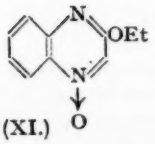

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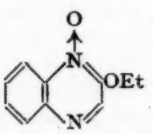

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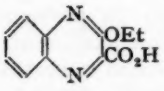
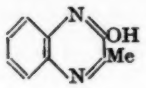


(XIII.)

Oxidation of 2-ethoxyquinoxaline-3-carboxylic acid (XIII) with hydrogen peroxide gave 2 : 3-dihydroxyquinoxaline in high yield and not the expected 2-hydroxy-3-ethoxyquinoxaline (IX). The reason for this became apparent when we treated 2-hydroxy-3-ethoxyquinoxaline with aqueous acetic acid, 2 : 3-dihydroxyquinoxaline being obtained in high yield.

2-Ethoxyquinoxaline-3-carboxylic acid was stable to aqueous acetic acid under the same conditions.



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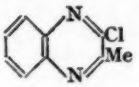

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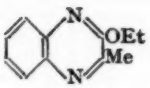

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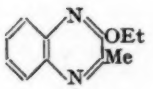
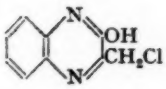
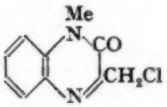


(XVII.)



(XVIII.)



(XIX.)

Treatment of 2-hydroxy-3-methylquinoxaline (XIV) (Hinsberg, *Annalen*, 1896, **292**, 245) with phosphoryl chloride gave 2-*chloro*-3-*methylquinoxaline* (XV) which was converted by the standard procedure into 2-*ethoxy*-3-*methylquinoxaline* (XVI). Hydrogen peroxide oxidation of the latter gave 3-*ethoxy*-2-*methylquinoxaline* 1-*oxide*, (XVII), which liberates iodine from acidified potassium iodide solution and on reduction with sodium dithionite (hydrosulphite) regenerates the parent 2-ethoxy-3-methylquinoxaline. Treatment of 3-ethoxy-2-methylquinoxaline 1-oxide with hydrochloric acid yields 2-*hydroxy*-3-*chloromethylquinoxaline* (XVIII) which is soluble in sodium hydroxide solution. 2-Hydroxy-3-chloromethylquinoxaline was characterised by methylation with methyl sulphate and alkali to the *monomethyl* derivative (XIX), and by its ultra-violet absorption spectrum in 0·1N-sodium hydroxide which is very similar to that of 2-hydroxy-3-methylquinoxaline :

	Max.$_1$, A.	ε.	Max.$_2$, A.	ε.
2-Hydroxy-3-methylquinoxaline	2380	23,600	3450	7450
2-Hydroxy-3-chloromethylquinoxaline	2405	26,000	3445	9000

Experimental.

2 : 3-*Dihydroxyquinoxaline.*—Meyer and Seeliger (*Ber.*, 1896, **29**, 2641) prepared 2 : 3-dihydroxyquinoxaline by treatment of *o*-phenylenediamine with ethyl oxalate; these authors do not give details of their preparation. The following method was found suitable. *o*-Phenylenediamine (10·8 g.) was heated with ethyl oxalate (60 g.) for 6 hours (bath temp. 160—170°). After cooling, the solid was collected and washed with ethanol and water. It was purified by dissolution in N-sodium hydroxide followed by filtration and acidification of the filtrate; 2 : 3-dihydroxyquinoxaline (68%) then separated as needles, m. p. > 360°. Light absorption in 0·1N-sodium hydroxide : Maxima at 3150 A. (ε = 12,000), 3260 A. (ε = 14,500), and 3400 A. (ε = 11,000). Scudi and Silber (*J. Biol. Chem.*, 1944, **156**, 343) give maxima at 3270 A. (ε = 16,800) and 3415 A. (ε = 10,600).

2 : 3-*Diketo*-1 : 4-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline.*—A solution of 2 : 3-dihydroxyquinoxaline (0·7 g.) in sodium hydroxide solution (2N ; 30 c.c.) was shaken at room temperature with methyl sulphate (3 c.c.) for 2 hours. The crystalline solid was collected, washed with water, and dried (0·51 g.; 62%); m. p. 255°. Crystallisation from ethanol gave 2 : 3-*diketo*-1 : 4-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline* as needles, m. p. 256—258° (Found : C, 63·1; H, 5·5; N, 14·7. $C_{10}H_{10}O_2N_2$ requires C, 63·2; H, 5·3; N, 14·7%).

2 : 3-*Dimethoxyquinoxaline.*—A solution of 2 : 3-dichloroquinoxaline (0·7 g.) in dry methanol (30 c.c.) was treated with a methanolic solution of sodium methoxide (from 0·2 g. of sodium and 10 c.c. of dry methanol), and the mixture refluxed for 1½ hours. 2 : 3-Dimethoxyquinoxaline (0·62 g.), m. p. 92—94°, was obtained as fine needles from methanol (Found : C, 62·9; H, 5·3; N, 14·8. Calc. for $C_{10}H_{10}O_2N_2$: C, 63·2; H, 5·3; N, 14·7%).

3-*Ethoxyquinoxaline* 1-*Oxide.*—A solution of 2-ethoxyquinoxaline (1 g.) in glacial acetic acid (30 c.c.) was treated with hydrogen peroxide solution (100 vol., 10 c.c.) and heated for 18 hours at 56°. The solution was evaporated under reduced pressure to a small bulk and the residue made just alkaline by the addition of potassium hydroxide solution. The mixture was extracted with chloroform (2 × 25 c.c.), the extract dried (Na_2SO_4), and evaporated. Crystallisation of the residue from *n*-hexane gave 3-*ethoxyquinoxaline* 1-*oxide* (0·6 g.) as needles, m. p. 104—106° (Found : C, 63·4; H, 5·6. $C_{10}H_{10}O_2N_2$ requires C, 63·2; H, 5·3%). The oxide is insoluble in water, N-sodium hydroxide, and N-hydrochloric acid, but dissolves in concentrated hydrochloric acid. It liberates iodine from potassium iodide solution in the presence of acetic acid using the procedure described by McIlwain (*loc. cit.*).

Hydrolysis. A solution of the oxide (0·25 g.) in ethanol (2 c.c.) and hydrochloric acid (2·5N ; 3 c.c.) was refluxed for 3½ hours, during which time solid separated. The ethanol was removed by distillation and the residue dissolved in 3N-sodium hydroxide. Acidification with dilute hydrochloric acid gave a crystalline precipitate of 2 : 3-dihydroxyquinoxaline, m. p. > 360° (0·17 g.). The absorption spectrum of this specimen in 0·1N-sodium hydroxide showed the characteristic triplet with principal maximum at 3250 A. (ε = 13,400). Methylation gave 2 : 3-diketo-1 : 4-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoxaline, m. p. 255—257° undepressed when mixed with an authentic specimen.

2-*Chloro*-3-*methylquinoxaline.*—2-Hydroxy-3-methylquinoxaline (Hinsberg, *Annalen*, 1896, **292**, 245)

(8 g.) was refluxed with freshly distilled phosphoryl chloride (50 c.c.) for 30 minutes. The solution was concentrated under reduced pressure and the residue treated with ice–water and the mixture extracted with ether. Removal of the ether from the dried (Na_2SO_4) extract followed by distillation gave the product as a red oil (b. p. 85°/0·5 mm.), solidifying to a crystalline mass (6·2 g., m. p. 84—86°). The colour could not be removed by crystallisation from light petroleum (b. p. 40—60°). A solution of the distillate (0·95 g.) in dry benzene (45 c.c.) was filtered through a column of activated alumina (75 × 15 mm.) and the column washed with benzene (135 c.c.). The colourless filtrate was evaporated and the residue crystallised from light petroleum (b. p. 40—60°) to yield *2-chloro-3-methylquinoxaline* as colourless needles, m. p. 86—87°. The compound sublimed rapidly at 85°/0·001 mm. (Found : C, 60·9; H, 4·0; N, 15·95. $C_9H_7N_2Cl$ requires C, 60·5; H, 3·9; N, 15·7%).

2-Ethoxy-3-methylquinoxaline.—A solution of 2-chloro-3-methylquinoxaline (4·8 g.) in dry ethanol (25 c.c.) was treated with a solution of sodium ethoxide in ethanol (from 1·1 g. of sodium and 35 c.c. of ethanol). The mixture was refluxed for 1 hour, filtered, and the filtrate evaporated. The residue was treated with water and the product isolated by means of ether. Crystallisation from *n*-hexane gave *2-ethoxy-3-methylquinoxaline* as needles, m. p. 55—57° (Found : C, 70·1; H, 6·5. $C_{11}H_{12}ON_2$ requires C, 70·2; H, 6·4%). The *picrate* separated as fine yellow needles from ethyl acetate, m. p. 116—118° (Found : C, 49·2; H, 3·5; N, 17·0. $C_{17}H_{15}O_8N_5$ requires C, 48·9; H, 3·6; N, 16·8%).

A solution of 2-ethoxy-3-methylquinoxaline (0·2 g.) in ethanol (2 c.c.) was refluxed for 1 hour with hydrochloric acid (3 c.c., 2·5N). The solution was concentrated, diluted with water, and the solid separating dissolved in N-sodium hydroxide. After filtration, the solution was acidified to litmus with hydrochloric acid and the precipitated solid collected. Crystallisation from aqueous ethanol gave 2-hydroxy-3-methylquinoxaline as needles, m. p. 245° not depressed when mixed with an authentic specimen (yield, 70%).

3-Ethoxy-2-methylquinoxaline 1-Oxide.—2-Ethoxy-3-methylquinoxaline (1·88 g.) in glacial acetic acid (40 c.c.) was treated with hydrogen peroxide solution (100 vol., 15 c.c.) and the mixture kept at 56° for 16 hours. The product was isolated by the method used for 3-ethoxyquinoxaline 1-oxide. Recrystallisation from light petroleum (b. p. 40—60°) gave *3-ethoxy-2-methylquinoxaline 1-oxide* (1·7 g.) as needles from dilute solution and plates from concentrated solution, m. p. 84—86°. It liberates iodine from potassium iodide solution in the presence of acetic acid (Found : 64·6; H, 5·8; N, 13·6. $C_{11}H_{12}O_2N_2$ requires C, 64·7; H, 5·9; N, 13·7%).

A solution of 3-ethoxy-2-methylquinoxaline 1-oxide (0·2 g.) in ethanol (5 c.c.) and water (5 c.c.) was heated under reflux with sodium dithionite (hydrosulphite) (0·25 g.) for 1 hour. More sodium hydrosulphite (0·25 g.) was added and the mixture again refluxed for 1 hour. Most of the ethanol was removed by distillation, and the mixture was treated with water and cooled; the separated oil then solidified. The solid was collected, dried, and crystallised from light petroleum to give 2-ethoxy-3-methylquinoxaline as needles, m. p. 51—53° not depressed when mixed with an authentic specimen. The picrate was obtained as fine yellow needles from ethyl acetate, m. p. 115—117° either alone or when mixed with the specimen previously described.

2-Hydroxy-3-chloromethylquinoxaline.—A solution of 3-ethoxy-2-methylquinoxaline 1-oxide (0·25 g.) in ethanol (2 c.c.) and 2·5N-hydrochloric acid (3 c.c.) was heated under reflux for 3½ hours. The mixture was diluted with water, cooled, and the solid, m. p. 265°, collected. The solid readily dissolved in cold N-sodium hydroxide and was precipitated by acidification of this solution with N-sulphuric acid. Crystallisation from a large volume of boiling water (charcoal) gave *2-hydroxy-3-chloromethylquinoxaline* as fine needles, m. p. 265—268° (Found : C, 55·2; H, 3·4; N, 14·2. $C_9H_7ON_2Cl$ requires C, 55·5; H, 3·6; N, 14·4%).

2-Keto-1-methyl-3-chloromethyl-1 : 2-dihydroquinoxaline.—A solution of 2-hydroxy-3-chloromethylquinoxaline (150 mg.) in N-sodium hydroxide (3 c.c.) was shaken at room temperature with methyl sulphate (0·5 c.c.). A solid (110 mg.) rapidly separated which after crystallisation from ethanol (charcoal) gave *2-keto-1-methyl-3-chloromethyl-1 : 2-dihydroquinoxaline* as needles, m. p. 228—230° (Found : C, 57·1; H, 4·1; N, 13·1. $C_{10}H_9ON_2Cl$ requires C, 57·5; H, 4·3; N, 13·4%).

2-Chloro-3-ethoxyquinoxaline.—A boiling solution of 2 : 3-dichloroquinoxaline (10 g.) in dry ethanol (200 c.c.) was treated with alcoholic sodium ethoxide solution (from 1·15 g. of sodium and 100 c.c. of ethanol) added dropwise with stirring over 6 hours. The mixture was refluxed for a further 1½ hours and kept overnight at room temperature. Salt was removed by filtration and the filtrate concentrated. The crystalline solid separating was recrystallised from ethanol from which *2-chloro-3-ethoxyquinoxaline* separated as fine needles, m. p. 71—73° (yield, 80%). For analysis, it was sublimed at 70°/10^{-3} mm. (Found : C, 57·5; H, 4·5. $C_{10}H_9ON_2Cl$ requires C, 57·55; H, 4·3%).

A solution of 2-chloro-3-ethoxyquinoxaline (1·0 g.) in a mixture of ethanol (20 c.c.) and hydrochloric acid (*d* 1·19; 5 c.c.) was heated on the water-bath for 1 hour. The solid separating was collected and identified as 2 : 3-dihydroxyquinoxaline by its light absorption in 0·1N-sodium hydroxide [maxima at 3140, 3270 (ε = 14,000) and 3400 A.] and by conversion into 2 : 3-diketo-1 : 4-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoxaline which separated as needles from methanol, m. p. 255—257° either alone or when mixed with an authentic specimen.

2-Hydroxy-3-ethoxyquinoxaline.—2-Chloro-3-ethoxyquinoxaline (1·0 g.) in ethanol (5 c.c.) was treated with 20% potassium hydroxide solution (10 c.c.) and the mixture refluxed for 4½ hours. The mixture was cooled and extracted with ether which removed unchanged material (200 mg.). The aqueous solution was acidified to litmus with dilute hydrochloric acid and the precipitated solid collected (dry weight, 550 mg.). Crystallisation from aqueous ethanol gave *2-hydroxy-3-ethoxyquinoxaline* as fine needles, m. p. 197—199° (Found : C, 62·85; H, 5·3; N, 14·9. $C_{10}H_{10}O_2N_2$ requires C, 63·2; H, 5·3; N, 14·7%). 2-Hydroxy-3-ethoxyquinoxaline (200 mg.) in glacial acetic acid (5 c.c.) and water (3 c.c.) was heated at 56° for 15 hours. Evaporation of the reaction mixture gave 2 : 3-dihydroxyquinoxaline (140 mg.) characterised by its absorption spectrum in 0·1N-sodium hydroxide [maxima at 3150, 3260 (ε = 14,500) and 3410 A.] and by formation of 2 : 3-diketo-1 : 4-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoxaline, m. p. 256—258° undepressed on admixture with an authentic specimen.

2 : 3-Dihydroxyquinoxaline by Hydrogen Peroxide Oxidation of Quinoxaline Derivatives.—A solution

of 2-hydroxyquinoxaline (1·46 g.) in glacial acetic acid (40 c.c.) was heated with hydrogen peroxide (100-vol., 15 c.c.) at 56° for 1½ hours, crystalline solid separating after 1 hour. The mixture was kept overnight at room temperature; the solid (dry weight 1·15 g.) was collected and dissolved in N-sodium hydroxide, acidification of the solution with N-hydrochloric acid giving 2 : 3-dihydroxyquinoxaline (1·15 g., 71%) as silky needles not melting below 340°. Light absorption in 0·1N-sodium hydroxide: Maxima at 3150 A. (ε = 12,200), 3260 A. (ε = 14,400), and 3410 A. (ε = 10,500).

Methylation of this specimen using the method described above gave 2 : 3-diketo-1 : 4-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoxaline as needles from methanol, m. p. 256—258° either alone or when mixed with an authentic specimen.

The general procedure adopted for the oxidation of 2-ethoxyquinoxaline-3-carboxylic acid, 2-hydroxyquinoxaline-3-carboxylic acid, quinoxaline-2 : 3-dicarboxylic acid, and 2-chloro-3-ethoxyquinoxaline was as follows. A mixture of the compound (0·5—0·8 g.), glacial acetic acid (20 c.c.), and hydrogen peroxide (10 c.c., 100-vol.) was kept at 56° for 16—20 hours. 2 : 3-Dihydroxyquinoxaline was isolated and characterised in each case by the method described above (yields, 65—85%).

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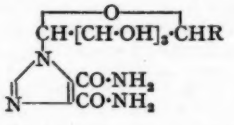
109. *Application of the Hofmann Reaction to the Synthesis of Heterocyclic Compounds. Part V. The Synthesis of* 9-D-*Mannopyranosidoxanthine and of* 9-D-*Ribopyranosidoxanthine.*

By R. A. BAXTER, A. C. MCLEAN, and F. S. SPRING.

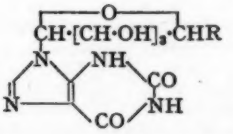
Using the methods developed in previous parts of this series, the xanthine-9-glycosides named in the title have been synthesised.

IN Part IV (Baxter and Spring, *J.*, 1947, 378) the preparation of 1-D-glucosido-, 1-D-arabinosido-, 1-L-arabinosido- and 1-D-xylopyranosido-glyoxaline-4 : 5-dicarboxyamide was described. Of these dicarboxyamides, only the last underwent intramolecular ring closure when treated with alkaline potassium hypobromite solution to yield the corresponding 9-substituted xanthine. We have now extended our study to other glycosides.

(I.)



(II.)



Treatment of the silver derivative of methyl glyoxaline-4 : 5-dicarboxylate with acetobromo-D-mannose gave a gum which could not be crystallised. Treatment of this with ammonia gave 1-D-*mannosidoglyoxaline*-4 : 5-*dicarboxyamide* (I, R = CH_2·OH) which on acetylation yielded 1-*tetra-acetyl*-D-*mannosidoglyoxaline*-4 : 5-*dicarboxyamide*. Treatment of 1-D-mannosidoglyoxaline-4 : 5-dicarboxyamide with alkaline potassium hypobromite gave 9-D-*mannopyranosidoxanthine* (II, R = CH_2·OH); this separates with water of crystallisation which was not lost on heating at 135° in a vacuum. Hydrolysis of the glycoside with dilute sulphuric acid gives a mixture of xanthine and D-mannose. The former was characterised by the preparation of its perchlorate and by its ultra-violet absorption spectrum, and the latter by the preparation of its phenylhydrazone. The ultra-violet absorption spectrum of 9-D-mannopyranosidoxanthine in both acid and alkali established the 9-location of the glycosidic group, and periodate oxidation showed this to be of the pyranose form.

Condensation of the silver derivative of methyl glyoxaline-4 : 5-dicarboxylate with acetobromo-D-ribose gave a syrup which, after treatment with methanolic ammonia followed by acetylation of the product with acetic anhydride in pyridine, yielded 1-*triacetyl*-D-*ribosidoglyoxaline*-4 : 5-*dicarboxyamide* which on treatment with methanolic ammonia yielded 1-D-*ribosidoglyoxaline*-4 : 5-*dicarboxyamide* (I, R = H). Treatment of this with alkaline potassium hypobromite solution followed by addition of alcohol to the reaction mixture precipitated a beautifully crystalline *potassium* salt of 9-D-ribosidoxanthine, which was characterised as a 9-riboside by its absorption spectrum. Hydrolysis of this salt with dilute sulphuric acid gave a mixture of xanthine (characterised by its absorption spectrum and by the preparation of its perchlorate) and ribose (characterised by the preparation of ribosazone). The potassium salt was converted into the corresponding lead salt which, when treated with hydrogen sulphide, gave 9-D-*ribopyranosidoxanthine* (II, R = H) which separates from aqueous alcohol with water of crystallisation; periodate oxidation shows the glycosidic group to be of the pyranose type.

Experimental.

1-D-*Mannosidoglyoxaline*-4 : 5-*dicarboxyamide*.—A suspension of the silver derivative of methyl glyoxaline-4 : 5-dicarboxylate (9·3 g.) in sulphur-free xylene (300 c.c.) was treated with a solution of freshly prepared acetobromo-D-mannose (from 15 g. of β-penta-acetyl D-mannose) in hot xylene (50 c.c.) and the mixture heated under reflux until the solution no longer gave a positive halogen test. Silver bromide was removed, and the filtrate, after cooling and removal of a small quantity of methyl glyoxaline-4 : 5-dicarboxylate, evaporated to dryness under reduced pressure. The residual syrup could not be crystallised. It was dissolved in methanol (45 c.c.) and the solution saturated with ammonia at 0° and kept at this temperature for 48 hours. The ammonia and some methanol were removed under reduced pressure and the crystalline solid collected and recrystallised from aqueous methanol to give 1-D-*mannosidoglyoxaline*-4 : 5-*dicarboxyamide* as needles, m.p. 208—210° (decomp.), $[\alpha]_D^{15°}$ −4° (*l*, 2; *c*, 1·3 in water) (Found : C, 41·8; H, 5·4; N, 17·5. $C_{11}H_{16}O_7N_4$ requires C, 41·8; H, 5·1; N, 17·7%).

1-*Tetra-acetyl*-D-*mannosidoglyoxaline*-4 : 5-*dicarboxyamide*.—A solution of 1-D-mannosidoglyoxaline-4 : 5-dicarboxyamide (1 g.) in pyridine (5 c.c.) and acetic anhydride (5 c.c.) was kept at 0° for 48 hours. The product was crystallised from aqueous ethanol to yield 1-*tetra-acetyl*-D-*mannosidoglyoxaline*-4 : 5-*dicarboxyamide* as small prisms (1 g.), m. p. 184—185° (Found : C, 47·4; H, 5·1; N, 11·6. $C_{19}H_{24}O_{11}N_4$ requires C, 47·1; H, 5·0; N, 11·6%).

9-D-*Mannosidoxanthine*.—1-D-Mannosidoglyoxaline-4 : 5-dicarboxyamide (1·0 g.) was treated at 0° with a freshly prepared alkaline solution of potassium hypobromite obtained as described in Part IV (5·6 c.c. ≡ 1 mol. of KOBr) and kept at this temperature for 1½ hours. The solution was heated on the steam-bath for a few minutes to decompose the excess hypobromite, and after cooling was acidified with acetic acid. After 16 hours at 0° the crystalline solid was collected (0·4 g.), a further small quantity (50 mg.) separating from the mother liquors on prolonged standing at 0°. After recrystallisation from aqueous ethanol 9-D-*mannosidoxanthine* was obtained as small elongated prisms which did not melt but partly decomposed between 300° and 360°. It gives an insoluble lead salt and a positive Molisch reaction. It is readily soluble in warm water but insoluble in the common organic solvents. $[\alpha]_D^{10°}$ +96° (*l*, 1; *c*, 0·5 in water) (Found : C, 37·4; H, 5·2; N, 16·3. $C_{11}H_{14}O_7N_4,2H_2O$ requires C, 37·7; H, 5·1; N, 16·0%). Light absorption : (*a*) In N/10-hydrochloric acid, maxima at 2350 A. (ε = 10,900) and 2610 A. (ε = 10,900); (*b*) in N/10-sodium hydroxide, maxima at 2490 A. (ε = 12,000), and 2770 A. (ε = 10,600).

Hydrolysis. The mannoside (200 mg.) was heated under reflux with N/2-sulphuric acid (7 c.c.). After 1 hour the separated xanthine was collected (75 mg.) and characterised by the preparation of the perchlorate which separated as plates, m.p. 257—258° (decomp.) either alone or when mixed with an authentic specimen. Light absorption in N/10-sodium hydroxide : Maximum at 2850 A. (ε = 8,600). The filtrate obtained after the separation of xanthine was exactly neutralised by the addition of sodium hydroxide solution and the solution treated with phenylhydrazine in aqueous acetic acid at 50° for 1 hour. After cooling the solid was collected and recrystallised from water to give D-mannose phenylhydrazone as microscopic prisms, m. p. 183° (decomp.) either alone or when mixed with an authentic specimen.

1-*Triacetyl*-D-*ribosidoglyoxaline*-4 : 5-*dicarboxyamide*.—β-Tetra-acetyl D-ribose (5 g.) (Levene and Tipson, *J. Biol. Chem.*, 1931, **92**, 109) was dissolved in glacial acetic acid (25 c.c.), saturated with dry hydrogen bromide at 0°, and kept at room temperature for 1 hour. The hydrogen bromide was removed at room temperature under reduced pressure, and the solution diluted with sulphur-free toluene (3 × 100 c.c.) and evaporated to a thick syrup, the temperature being maintained below 35°. This syrup crystallised to yield acetobromo-D-ribose as prisms from ether–light petroleum (b. p. 40—60°), m. p. 96°. Since we found that the crystalline acetobromo-sugar quickly decomposed on attempted dissolution in hot xylene, it was advantageous to use the crude syrup which is more readily soluble in xylene. A solution of the syrup (from 5 g. of tetra-acetyl D-ribose) in sulphur-free xylene (100 c.c.) was added to a suspension of the silver derivative of methyl glyoxaline-4 : 5-dicarboxylate (from 3·1 g. of methyl glyoxaline-4 : 5-dicarboxylate). The mixture was boiled for 10 minutes, after which the solution no longer gave a positive halogen test. The cooled mixture was filtered, and the filtrate evaporated under reduced pressure to yield a thick syrup. The syrup was dissolved in methanol (100 c.c.), and the solution saturated with dry ammonia at 0° and kept for 24 hours at room temperature. Evaporation of this solution gave a syrup which failed to crystallise. It was dissolved in dry pyridine (15 c.c.) and acetic anhydride (15 c.c.), and kept at 0° for 12 hours. Ethanol (50 c.c.) was added with cooling, and the mixed solvents were removed under reduced pressure; the residue then crystallised. Recrystallisation from ethanol yielded 1-*triacetyl*-D-*ribosidoglyoxaline*-4 : 5-*dicarboxyamide* as prismatic needles, m. p. 246—248°, $[\alpha]_D^{17°}$ +55° (*l*, 1; *c*, 2·0 in chloroform) (Found : C, 47·1; H, 5·0; N, 13·2. $C_{16}H_{20}O_9N_4$ requires C, 46·6; H, 4·9; N, 13·6%).

1-D-*Ribosidoglyoxaline*-4 : 5-*dicarboxyamide*.—The triacetyl-D-riboside (1 g.) was deacetylated by treatment with methanolic ammonia in the usual manner. 1-D-*Ribosidoglyoxaline*-4 : 5-*dicarboxyamide* separated from aqueous ethanol as needles (0·65 g.), m. p. 215—216°, $[\alpha]_D^{17°}$ +17° (*l*, 1; *c*, 1·0 in water). It is readily soluble in water and insoluble in ethanol (Found : C, 42·0; H, 5·1. $C_{10}H_{14}O_6N_4$ requires C, 42·0; H, 4·9%).

9-D-*Ribosidoxanthine*.—1-D-Ribosidoglyoxaline-4 : 5-dicarboxyamide (0·5 g.) was shaken with potassium hypobromite solution (2·7 c.c.) at 0°. After 1 hour at 0°, a few drops of alcohol were added, the potassium salt of 9-D-ribosidoxanthine (200 mg.) separating as needles which, after recrystallisation from aqueous ethanol, had m. p. 295—300° (decomp.), $[\alpha]_D^{16°}$ −12° (*l*, 1; *c*, 1·0 in water) (Found : C, 33·8; H, 4·1; N, 15·3, 15·9. $C_{10}H_{11}O_6N_4K,2H_2O$ requires C, 33·5; H, 4·2; N, 15·6%). The potassium salt (100 mg.) in water (5 c.c.) was treated dropwise with a saturated solution of lead acetate and dilute ammonia until no further precipitate formed with either reagent. The lead salt was collected, washed with water, suspended in hot water (100 c.c.), and decomposed by a stream of hydrogen sulphide. The precipitate was filtered, and the solid again suspended in water and treated with hydrogen sulphide. The combined filtrates were evaporated to 5 c.c. bulk, and the solution was diluted with ethanol (5 c.c.) and kept at 0°; 9-D-*ribosidoxanthine* then separated as fine needles (48 mg.) which did not melt below

360°, $[\alpha]_D^{18°}$ −10° (*l*, 1; *c*, 0·3 in water) (Found: C, 39·9; H, 4·9; N, 18·1. $C_{10}H_{12}O_6N_4,H_2O$ requires C, 39·7; H, 4·6; N, 18·5%). Light absorption: (*a*) In N/10-sodium hydroxide, maxima at 2490 A. (ε = 11,000) and 2780 A. (ε = 9,600); (*b*) in N/10-hydrochloric acid, maxima at 2340 A. (ε = 10,400) and 2620 A. (ε = 10,400).

Hydrolysis. The potassium salt of 9-D-ribosidoxanthine (70 mg.) was refluxed with N/2-sulphuric acid (5 c.c.) for 2 hours. The separated xanthine (20 mg.) was collected and characterised by the preparation of the perchlorate, m. p. and mixed m. p. 260°, and by its ultra-violet light absorption in N/10-sodium hydroxide solution (maximum at 2840 A., ε = 9,400). The filtrate obtained after the removal of xanthine was exactly neutralised with sodium carbonate solution and treated with excess of phenylhydrazine in dilute acetic acid; ribosazone (10 mg.) separated as micro-needles, m.p. 160—162° not depressed when mixed with an authentic specimen.

Periodate Oxidations.—The oxidations were carried out as described in Part IV.

Compound.	Formic acid (mols. per mol.).	Periodate consumed (mols. per mol.).
9-D-Mannosidoxanthine	1·05	2·0
1-D-Ribosidoglyoxaline-4 : 5-dicarboxyamide	1·0	2·08
9-D-Ribosidoxanthine	1·06	2·04

The authors thank Professor A. R. Todd, F.R.S., for the gift of a liberal supply of D-ribose, and gratefully acknowledge the award of a Fellowship (to A. C. McL.) by the Ferguson Bequest Fund.

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110. *The Synthesis of Some Aryl 2-Thienyl Sulphones and the Nitration of Thiophen-2-sulphonyl Chloride.*

By H. BURTON and W. A. DAVY.

Alternative methods for the synthesis of aryl 2-thienyl sulphones (and sulphides) have been investigated. The Friedel–Crafts method using thiophen-2-sulphonyl chloride appeared to be satisfactory for aryl = phenyl, but interaction of thiophen-2-sulphinic acid with aryl iodides proceeded slowly or not at all. Nitration of thiophen-2-sulphonyl chloride was reinvestigated; the 4-nitro-derivative was obtained pure.

IN attempts to synthesise aryl 2-thienyl sulphones and related compounds structurally similar to 4 : 4′-diaminodiphenyl sulphone and sulphanilamide, we have examined various synthetic methods. We avoided using thiophen itself as a starting material since it is well known that profound decomposition of this compound usually occurs under the action of acids and metal salts. Thiophen-2-sulphonyl chloride (Steinkopf and Höpner, *Annalen*, **1933**, **501**, 174) being readily available, we first investigated its reaction with resorcinol dimethyl ether in presence of zinc chloride (see Burton and Hoggarth, *J.*, **1945**, 14); this resulted in the formation of a small amount of the expected 2 : 4-*dimethoxyphenyl 2-thienyl sulphone*. We assign this constitution since the compound gave the correct analysis and differed from the alternative reaction product, *viz.*, m-*methoxyphenyl thiophen-2-sulphonate*. Since 2-iodothiophen did not react with sodium 2 : 4-dimethoxythiophenoxide we could not verify the constitution.

The Friedel–Crafts reaction between thiophen-2-sulphonyl chloride and benzene proceeded fairly satisfactorily giving a 55% yield of *phenyl 2-thienyl sulphone* (as expected, benzenesulphonyl chloride and thiophen gave tars), which could also be obtained by oxidation of *phenyl 2-thienyl sulphide*. This sulphide was formed in a somewhat impure state by treating 2 : 2′-dithienyl disulphide (Challenger and Miller, private communication) with phenylmagnesium bromide in benzene.

2-Iodothiophen did not react with potassium *p*-acetamidobenzenesulphinate, and use of the more reactive silver salt (Bambas, *J. Amer. Chem. Soc.*, **1945**, **67**, 668) gave only traces of the acetyl derivative of the required p-*aminophenyl 2-thienyl sulphone*. An alternative route to this compound *via* p-*nitrophenyl 2-thienyl sulphone* was no more successful, since we found that 2-thienylthiol and *p*-chloronitrobenzene in an alkaline medium gave very little p-*nitrophenyl 2-thienyl sulphide*.

We then explored the possibility of using thiophen-2-sulphinic acid which is readily prepared in good yield by the sodium sulphite reduction of the 2-sulphonyl chloride. The acid reacted rapidly with *p*-benzoquinone to give 2 : 5-*dihydroxyphenyl 2-thienyl sulphone*, slowly (as the potassium salt) with methyl iodide to form 2-*thienyl methyl sulphone*, but not at all with *p*-chloronitrobenzene.

In view of the well-known reaction between an arylsulphenyl chloride and a reactive molecule (for references see Burton and Davy, *J.*, **1947**, 52), we attempted to prepare thiophen-2-sulphenyl

chloride by the action of chlorine on 2 : 2′-dithienyl disulphide in chloroform. The typical colour change from pale yellow to orange was observed, but all attempts to condense the supposed sulphenyl chloride with resorcinol were unsuccessful. Dark tarry products were always obtained, and no crystalline product was obtainable even after acetylation.

The action of fuming nitric acid on thiophen-2-sulphonyl chloride is known (Steinkopf and Höpner, *loc. cit.*) to give a mixture of the 4- and 5-nitro-derivatives in the ratio of about 8 : 3. This ratio was deduced from the relative amounts of the known 3- and 2-nitrothiophen respectively obtained by desulphonation of the mixed sulphonic acids with superheated steam. Fractional distillation of the nitration mixture has now resulted in the separation of the crystalline *4-nitrothiophen-2-sulphonyl chloride* which is concentrated in the higher-boiling fractions. Hydrolysis followed by desulphonation then gave 3-nitrothiophen in at least 64% yield thus establishing the constitution. We consider the alternative structure, namely 3-nitrothiophen-2-sulphonyl chloride (which would similarly give 3-nitrothiophen), as excluded, since formation of this would necessitate substitution of a nitro-group *ortho* to the sulphonyl chloride group. This chloride led to *4-nitrothiophen-2-sulphonamide* which was reduced to the *4-amino-amide*. 5-Nitrothiophen-2-sulphonyl chloride was not obtained absolutely pure (see experimental section) and although the *nitro-amide* could be prepared satisfactorily attempted reduction of this caused profound decomposition.

Experimental.

Thiophen-2-sulphonyl chloride was prepared in 50% yield by Steinkopf and Höpner's method (*loc. cit.*). It had b. p. 131—132°/20 mm. and m. p. 32°, after crystallisation from ligroin. The colourless plates turned green after being kept for more than about a week.

2 : 4-*Dimethoxyphenyl 2-Thienyl Sulphone.*—An intimate mixture of thiophen-2-sulphonyl chloride (9·2 g.), resorcinol dimethyl ether (6·9 g.), and powdered, anhydrous zinc chloride (6·8 g.) was heated at 105° until effervescence ceased. The tarry reaction mixture was heated with concentrated hydrochloric acid (50 c.c.) and water (50 c.c.) and then extracted with benzene. The small amount of residue from the dried ($CaCl_2$) benzene extract solidified on trituration with cold methyl alcohol and crystallised (charcoal) from butyl alcohol, giving the *sulphone* as colourless needles, m. p. 128—129° (Found: C, 50·9; H, 4·3; S, 22·9. $C_{12}H_{12}O_4S_2$ requires C, 50·7; H, 4·2; S, 22·5%).

m-*Methoxyphenyl Thiophen-2-sulphonate.*—Thiophen-2-sulphonyl chloride (9·2 g.) and *m*-methoxyphenol (6·2 g.) were dissolved in pyridine (25 c.c.) and the mixture was kept overnight. Filtration from pyridine hydrochloride and extraction with ether gave, after washing with dilute hydrochloric acid and drying ($CaCl_2$), the *ester* (7 g.) which separated from alcohol–ligroin in colourless needles, m. p. 51—53° (Found: C, 48·8; H, 3·8; S, 24·2. $C_{11}H_{10}O_4S_2$ requires C, 48·9; H, 3·7; S, 23·7%).

2 : 4-Dimethoxythiophenol, b. p. 138—140°/15 mm., was obtained in 30% yield by reduction of 2 : 4-dimethoxybenzenesulphonyl chloride with zinc dust and dilute sulphuric acid. The oil gradually deposited crystals of *di*-2 : 4-*dimethoxyphenyl disulphide* which crystallised from alcohol in colourless plates, m. p. 117° (Found: C, 56·9; H, 5·9; S, 18·4; *M*, 338. $C_{16}H_{18}O_4S_2$ requires C, 56·8; H, 5·3; S, 18·9%; *M*, 338).

Phenyl 2-Thienyl Sulphone.—(*a*) Aluminium chloride (3·5 g.) was added gradually to thiophen-2-sulphonyl chloride (4·6 g.) in benzene (20 c.c.) at room temperature. After 15 minutes the black mixture was added with stirring to warm dilute hydrochloric acid. The benzene layer on evaporation under reduced pressure gave the *sulphone* (3·1 g.) which crystallised from alcohol in colourless flattened needles, m. p. 123° (Found: C, 53·7; H, 3·7; S, 28·7. $C_{10}H_8O_2S_2$ requires C, 53·6; H, 3·6; S, 28·6%).

Attempted preparation from benzenesulphonyl chloride (17·65 g.), thiophen (8·4 g.), and aluminium chloride (15 g.) at 35—40° gave a black tar.

(*b*) A solution of 2 : 2′-dithienyl disulphide (7·1 g.; 0·03 mol.) in benzene (75 c.c.) was added slowly, with cooling and stirring, to ethereal phenylmagnesium bromide (0·1 mol.). The pale brown solution was then boiled on the steam-bath, the ether being allowed to evaporate, and benzene (100 c.c.) added. After boiling for 18 hours the mixture was decomposed with ice and ammonium chloride. Fractionation of the dried benzene layer gave: (i) diphenyl, b. p. 120—140°/20 mm., m. p. and mixed m. p. 70° after crystallisation from alcohol, (ii) a fraction (3·9 g.), b. p. 155—160°/20 mm., which redistilled almost entirely at 155—157°/15 mm. This was impure *phenyl 2-thienyl sulphide* (Found: S, 28·5. $C_{10}H_8S_2$ requires S, 33·3%).

The sulphide (1·07 g.), 30% hydrogen peroxide (0·7 c.c.), and acetic acid (10 c.c.) were mixed and kept at room temperature overnight. The mixture was diluted with water and then extracted with warm ligroin (b. p. 40—60°). The extract was washed with dilute sodium hydrogen carbonate, dried ($CaCl_2$), and evaporated; the residual *phenyl 2-thienyl sulphoxide* crystallised from ligroin (b. p. 40—60°) in colourless hair-like needles, m. p. 69—70° (Found: C, 58·0; H, 4·2; S, 30·9. $C_{10}H_8OS_2$ requires C, 57·7; H, 3·8; S, 30·8%).

The sulphide (1·0 g.) and 30% hydrogen peroxide (1·5 c.c.) in acetic acid (15 c.c.) were heated on the steam-bath for 45 minutes. Addition of water to the cold solution precipitated the sulphone, m. p. and mixed m. p. 124°, unaltered by three crystallisations from alcohol (Found: C, 53·3; H, 3·8; S, 28·7%).

p-*Aminophenyl 2-Thienyl Sulphone.*—2-Iodothiophen (8·4 g.) and silver *p*-acetamidobenzenesulphinate (12·5 g.) in alcohol (80 c.c.) and water (50 c.c.) were refluxed for 20 hours. After removal of the alcohol by evaporation the residue was extracted twice with ether and the combined ethereal extracts were washed successively with dilute sodium thiosulphate and water. The dried (Na_2SO_4) extract yielded a small amount of *p*-acetamidophenyl 2-thienyl sulphone which crystallised from aqueous alcohol in colourless, minute crystals, m. p. 106° (decomp.). Hydrolysis with 5N-hydrochloric acid at 95° gave,

after crystallisation from alcohol, the *sulphone* (0·1 g.) in colourless needles, m. p. 134° (Found : C, 50·5; H, 4·5; N, 6·1; S, 26·7. $C_{10}H_9O_2NS_2$ requires C, 50·2; H, 3·8; N, 6·0; S, 26·8%).

p-*Nitrophenyl* 2-*Thienyl Sulphone.*—2 : 2′-Dithienyl disulphide (2·5 g.) in alcohol (10 c.c.) was treated with glucose (2·5 g.) in water (5 c.c.) followed by sodium hydroxide (2·5 g.) in water (5 c.c.). The mixture soon became hot and gave a clear solution. After being heated on the steam-bath for 5 minutes the dark brown solution was added to *p*-chloronitrobenzene (4·1 g.) in alcohol (10 c.c.). After 30 hours' boiling the alcohol was evaporated and the residue extracted with ether. The residue from the dried (K_2CO_3) extract gradually deposited crystals which separated from alcohol (charcoal) in bright yellow needles (0·1 g.). p-*Nitrophenyl* 2-*thienyl sulphide* had m. p. 62° depressed by admixture with either *p*-chloronitrobenzene or 2 : 2′-dithienyl disulphide (Found : C, 51·3; H, 3·0; N, 5·9; S, 26·6. $C_{10}H_7O_2NS_2$ requires C, 50·6; H, 3·0; N, 5·9; S, 27·0%).

Oxidation of the sulphide with 30% hydrogen peroxide in acetic acid at 100° gave the *sulphone* which crystallised from alcohol in colourless plates, m. p. 139° (Found : N, 5·4; S, 23·5. $C_{10}H_7O_4NS_2$ requires N, 5·2; S, 23·8%).

Thiophen-2-sulphinic Acid.—Thiophen-2-sulphonyl chloride (18·25 g.) was shaken mechanically with a solution of crystalline sodium sulphite (62·5 g.) in water (125 c.c.), the mixture being kept slightly alkaline to phenolphthalein by the frequent addition of a few drops of 50% sodium hydroxide solution. After 1½ hours the mixture was filtered, acidified with cold 60% sulphuric acid, and extracted with two successive portions of ether (100 c.c.). The combined extracts were dried ($CaCl_2$) and evaporated; the pale yellow oil rapidly solidified in a vacuum desiccator to a crystalline mass, m. p. 72—73° (Weitz, *Ber.*, 1884, **17**, 800, gives m. p. 67°). The acid decomposes slowly when kept at room temperature.

2 : 5-*Dihydroxyphenyl* 2-*Thienyl Sulphone.*—*p*-Benzoquinone (0·54 g.) in warm water (15 c.c.) was added to thiophen-2-sulphinic acid (0·75 g.) in water (10 c.c.). Solid was precipitated immediately and the yellow colour of the quinone discharged. The *sulphone* (1·16 g.) crystallised from water containing a little alcohol in colourless plates, m. p. 186° (Found : S, 25·2. $C_{10}H_8O_4S_2$ requires S, 25·0%).

2-*Thienyl Methyl Sulphone.*—A mixture of thiophen-2-sulphinic acid (2·96 g.), potassium hydroxide (1·12 g.), water (20 c.c.), methyl iodide (3 g.), alcohol (10 c.c.), and traces of iodine and copper powder was boiled for 27 hours. After filtration the alcohol was evaporated and the slightly acidic residue made alkaline with sodium carbonate. The *sulphone* solidified; it crystallised from aqueous alcohol in colourless plates (0·73 g.), m. p. 47° (Found : C, 36·6; H, 3·95; S, 39·3. $C_5H_6O_2S_2$ requires C, 37·0; H, 3·7; S, 39·5%).

Nitration of Thiophen-2-sulphonyl Chloride.—The chloride (27 g.) was added gradually during 1 hour to well-stirred fuming nitric acid (110 c.c.) at 25—30°. After being stirred for 2 hours at 40° the mixture was added to crushed ice (350 g.), and the oily product extracted with carbon tetrachloride. Evaporation of the dried ($CaCl_2$) extract gave the mixed nitrothiophen-2-sulphonyl chlorides (26 g.). Distillation then gave two fractions, b. p. 130—134°/0·9 mm. and 135—140°/0·9 mm. When kept, the latter fraction solidified almost completely to pale yellow crystals, m. p. 42—44°, which turned orange when exposed to light. Recrystallisation from benzene–ligroin (b. p. 60—80°) gave 4-*nitrothiophen-2-sulphonyl chloride* in almost colourless long prisms, m. p. 48°, unchanged by further crystallisation (Found : N, 6·2. $C_4H_2O_4NClS_2$ requires N, 6·15%). A small amount of the same chloride also crystallised from the first fraction and was separated by filtration.

Hydrolysis of this chloride (0·8 g.) by boiling water (4 c.c.) for 1½ hours followed by the addition of water (5 c.c.) and concentrated sulphuric acid (7 c.c.) and distillation in superheated steam gave, at 130—150° (temperature of reaction mixture), 3-nitrothiophen (0·29 g.; 64%), m. p. 74—76°, after crystallisation from alcohol.

4-*Nitrothiophen-2-sulphonamide.*—In initial experiments the oily mixture of nitrothiophen-2-sulphonyl chlorides was added slowly to a mixture of acetone (20 c.c.) and aqueous ammonia (*d* 0·88) (20 c.c.) at 5—10°. After filtration from ammonium chloride the acetone solution was evaporated to dryness and the residue crystallised from water. Fractional crystallisation from butyl alcohol gave a dark brown crystalline product, m. p. 156—157°, unchanged by further crystallisation.

The solid chloride (above) (4·8 g.) in acetone (15 c.c.) was added slowly to a cold saturated solution of ammonia in acetone (75 c.c.) and the mixture again saturated with ammonia. Filtration, followed by evaporation of the acetone under reduced pressure, gave an oil which solidified on being stirred with water. The *sulphonamide* (2·4 g.) crystallised from water in pale brown, lustrous plates, m. p. 164°, unchanged by further crystallisation (Found : N, 13·9. $C_4H_4O_4N_2S_2$ requires N, 13·5%).

5-*Nitrothiophen-2-sulphonamide.*—The liquid nitrothiophen-2-sulphonyl chloride left after removal of the solid isomer, m. p. 48°, was refractionated and the lower-boiling material, from which no solid separated, was hydrolysed and desulphonated as above. A very small amount of 3-nitrothiophen distilled at 135—145°, but at 150—175° the distillate consisted entirely of 2-nitrothiophen, m. p. 43—44°.

Treatment of the liquid chloride with ammonia in acetone as described above gave the *sulphonamide*, almost colourless plates from water, m. p. 136° (Found : N, 13·2. $C_4H_4O_4N_2S_2$ requires N, 13·5%).

4-*Aminothiophen-2-sulphonamide.*—The nitrosulphonamide, m. p. 164°, was reduced with hydrogen in the presence of Raney nickel and absolute alcohol at ordinary temperature and pressure. Evaporation of the alcoholic solution under reduced pressure to a small volume and addition of ligroin (b. p. 60—80°) gave the *amino-sulphonamide* in colourless, flattened needles, m. p. 133° (decomp.), unchanged by recrystallisation from alcohol–ligroin (Found : C, 27·2; H, 3·5; N, 15·7; S, 36·3. $C_4H_6O_2N_2S_2$ requires C, 27·0; H, 3·4; N, 15·7; S, 36·0%).

5-Aminothiophen-2-sulphonamide was obtained similarly as an amorphous solid, m. p. 116—118° (decomp.), which could not be obtained crystalline. A crystalline benzoyl derivative could not be prepared.

We thank Imperial Chemical Industries Limited for a grant to one of us (W. A. D.) and also for the gift of chemicals, and Professor F. Challenger for a gift of thiophen.

THE UNIVERSITY, LEEDS, 2. [*Received, May 9th*, 1947.]

111. *The Use of Phenylmagnesium Bromide for the Preparation of Phenyl Aryl Sulphides, Sulphoxides, and Sulphones.*

By H. Burton and W. A. Davy.

Phenyl aryl sulphides are obtained in moderate yields from diaryl disulphides and phenylmagnesium bromide (I). In agreement with Gilman and Fothergill (*J. Amer. Chem. Soc.*, 1929, **51**, 3501), phenyl aryl sulphones or sulphoxides are formed from arysulphonyl chlorides and (I) according to the experimental conditions; when the arylsulphonyl chloride (*e.g.*, thiophen-2-sulphonyl chloride) is relatively unstable, a preponderating reaction appears to be the formation of diphenyl sulphoxide. The same side-reaction occurs to a very minor extent with the stable *p*-toluenesulphonyl chloride.

The limited applicability of the usual methods for the synthesis of aryl 2-thienyl sulphones (Burton and Davy, preceding paper) prompted us to explore the possibility of using the Grignard reagent for this purpose, more especially since little work has been reported in this field. We have reported (*loc. cit.*) that phenylmagnesium bromide (I) and 2 : 2′-dithienyl disulphide gave a moderate yield of phenyl 2-thienyl sulphide, and we have found that phenyl *p*-tolyl sulphide is formed in similar yield using di-*p*-tolyl disulphide and (I). Preliminary work using 4 : 4′-dinitrodiphenyl and 4 : 4′-diacetamidodiphenyl disulphides showed that whilst the former reacted vigorously with (I) the product was a black tar (a similar product was obtained also using *p*-nitrobenzenesulphenyl chloride), whereas the diacetamido-compound was recovered unchanged, even when the reaction was carried out in a large volume of anisole to effect solution. *p*-Acetamidobenzenesulphenyl chloride and (I) gave an almost quantitative yield of 4 : 4′-diacetamidodiphenyl disulphide.

The interaction of various arylsulphonyl chlorides with Grignard reagents has been studied chiefly by Hepworth and Clapham (*J.*, 1921, **119**, 1188), Wedekind and Schenk (*Ber.*, 1921, **54**, 1604), and Gilman and Fothergill (*J. Amer. Chem. Soc.*, 1929, **51**, 3501). The last-named authors criticised the findings of the earlier workers and postulated the following reactions to account for the results:

(i) $Ar{\cdot}SO_2Cl + MgPhBr \longrightarrow Ar{\cdot}SO_2Ph + MgBrCl$;
(ii) $Ar{\cdot}SO_2Cl + MgPhBr \longrightarrow Ar{\cdot}SO_2{\cdot}MgBr + PhCl$;
(iii) $Ar{\cdot}SO_2{\cdot}MgBr + MgPhBr \longrightarrow Ar{\cdot}SOPh + (MgBr)_2O$.

Reactions (i) and (ii) occur in the cold, but in the hot (ii) followed by (iii) takes place. We have confirmed that these changes do occur in the reaction between *p*-toluenesulphonyl chloride and (I); in particular we have shown that phenyl *p*-tolyl sulphoxide is formed from *p*-toluenesulphinic acid and (I). We prefer to postulate reaction (iii) thus:

$$Ar{\cdot}SO_2{\cdot}MgBr + MgPhBr \longrightarrow Ar{\cdot}SPh(OMgBr)_2 \longrightarrow Ar{\cdot}SPh(OH)_2 \longrightarrow Ar{\cdot}SOPh + H_2O.$$

The reactions of *p*-toluenesulphinyl chloride with (I) appear to run parallel with those of the sulphonyl chloride and give phenyl *p*-tolyl sulphoxide and sulphide.

We then decided to explore the possibility of synthesising phenyl 2-thienyl sulphone or sulphoxide by using either thiophen-2-sulphonyl chloride (II) and (I) or, alternatively, 2-thienylmagnesium iodide and benzenesulphonyl chloride. We were finally forced to use (II) since this was the only thiophen derivative we possessed, and we could not obtain a further supply of thiophen. Interaction of (I) and (II) in boiling benzene gave a compound, m. p. 69°, which depressed the m. p. (69—70°) of phenyl 2-thienyl sulphoxide (Burton and Davy, *loc. cit.*) and contained much too little sulphur. In fact, the compound analysed as an impure specimen of diphenyl sulphoxide and did not depress the m. p. (70°) of an authentic specimen of this. The compound, m. p. 69°, was oxidised by hydrogen peroxide to a sulphone, m. p. 124°, which did not depress the m. p. of either phenyl 2-thienyl sulphone or diphenyl sulphone; genuine specimens of these sulphones do not undergo m. p. depression. We have repeated the reaction between (I) and (II) several times; on each occasion a sulphoxide, m. p. 69°, oxidisable to a sulphone, m. p. 124°, was obtained. Analytical data for these compounds, however, showed some degree of divergence but they could all be explained on the assumption that the sulphoxide, m. p. 69°, was diphenyl sulphoxide containing a small amount of phenyl 2-thienyl sulphoxide.

These results led us to examine in further detail the phenyl *p*-tolyl sulphoxide produced from *p*-toluenesulphonyl chloride and (I). Fractional crystallisation of the crude reaction product from ligroin showed the undoubted presence of a very small amount of diphenyl sulphoxide. We suggest that the following reactions would account for the formation of the diphenyl sulphoxide:

$Ar{\cdot}SO_2{\cdot}MgBr + MgPhBr \longrightarrow Ar{\cdot}MgBr + Ph{\cdot}SO_2{\cdot}MgBr$;
$Ph{\cdot}SO_2{\cdot}MgBr + MgPhBr \longrightarrow Ph_2SO$ [cf. (iii) above].

It is probable that the relative stability of the sulphonyl chloride (or sulphinic acid) may determine the amount of diphenyl sulphoxide produced in such reactions. It is hoped to present further evidence on this point later.

Experimental.

Reaction between Phenylmagnesium Bromide and Di-p-tolyl Disulphide.—Di-*p*-tolyl disulphide (12·3 g.; 0·05 mol.) in benzene (100 c.c.) was added gradually with stirring to ethereal phenylmagnesium bromide (0·15 mol.). The ether was then distilled off, benzene (50 c.c.) added, and the mixture boiled for 22 hours. Decomposition with ice and ammonium chloride, separation of the benzene layer, and extraction with benzene gave, after drying and distillation, two fractions: (i) b. p. 90—100°/20 mm., (ii) up to 180°/20 mm. Fraction (i) solidified when cooled, and crystallisation from alcohol gave colourless plates (1·5 g.), m. p. 43—44°, presumably of thio-*p*-cresol. Fraction (ii) (6·5 g.) was redistilled, b. p. 170—172°/15 mm., and then oxidised with 30% hydrogen peroxide (9·5 c.c.) in acetic acid (20 c.c.) at 100° for 40 minutes; phenyl *p*-tolyl sulphone (6·1 g.), m. p. and mixed m. p. 124—125°, crystallised when the solution was cooled.

Reaction between Phenylmagnesium Bromide and p-*Toluenesulphonyl Chloride.*—(a) *In the cold.* *p*-Toluenesulphonyl chloride (57·3 g.; 0·3 mol.) in ether (200 c.c.) was added slowly with stirring to ethereal phenylmagnesium bromide (0·3 mol.) at − 10° to − 5°. After being stirred for a further 30 minutes at − 5° the mixture was decomposed with cold, dilute hydrochloric acid. The ether layer was separated and the aqueous solution extracted with ether. Dilute sodium hydroxide extracted *p*-toluenesulphinic acid (20·5 g.) from the combined ethereal extracts. The remaining ether-soluble product was steam distilled, yielding chlorobenzene (10 g.), b. p. 45°/30 mm., and diphenyl (7·5 g.) as volatile products, and phenyl *p*-tolyl sulphone (9·6 g.), m. p. and mixed m. p. 125°, as the non-volatile product. *p*-Toluenesulphinic was identified by m. p. and mixed m. p., and chlorobenzene was characterised as its 2 : 4-dinitro-derivative.

(b) *In the hot.* *p*-Toluenesulphonyl chloride (19·1 g.; 0·1 mol.) in benzene (100 c.c.) was added during 1 hour with stirring to cooled ethereal phenylmagnesium bromide (0·3 mol.). The ether was then evaporated, replaced by benzene (100 c.c.), and the mixture refluxed for 22 hours. Decomposition with dilute hydrochloric acid and extraction of the aqueous layer with ether gave a benzene–ether extract which yielded a trace of phenol when extracted with dilute sodium hydroxide. Steam distillation of the residue from this extract gave chlorobenzene (6·7 g.) and diphenyl (6·6 g.) as the volatile products, and left phenyl *p*-tolyl sulphoxide (13·5 g.; 62%), b. p. 205—207°/10 mm., m. p. and mixed m. p. 71—72° after crystallisation from ligroin (b. p. 40—60°).

The sulphoxide was oxidised by 30% hydrogen peroxide in hot acetic acid to phenyl *p*-tolyl sulphone, m. p. and mixed m. p. 124—125°.

Phenyl *p*-tolyl sulphoxide was similarly obtained using benzenesulphonyl chloride and *p*-tolylmagnesium bromide.

Reaction between Phenylmagnesium Bromide and p-*Toluenesulphinic Acid.*—*p*-Toluenesulphinic acid (9·3 g.; 0·06 mol.) in ether (350 c.c.) was added slowly with stirring to cold ethereal phenylmagnesium bromide (0·18 mol.); a colourless solid separated during the addition. Benzene (400 c.c.) was added and the ether evaporated. After refluxing for 19 hours and working up in the usual manner, phenyl *p*-tolyl sulphoxide (6·6 g.; 51%) was obtained. No unchanged sulphinic acid could be isolated.

p-*Toluenesulphinyl Chloride and its Reaction with Phenylmagnesium Bromide.*—Dry *p*-toluenesulphinic acid (12 g.) was treated dropwise with freshly distilled thionyl chloride (15 g.). After the initial effervescence had ceased the mixture was heated on the steam-bath for 15 minutes and the excess of thionyl chloride removed under reduced pressure, first at room temperature and then at 50°. Extraction of the residue with boiling ligroin (b. p. 40—60°) (100 c.c.) and evaporation of the extract under reduced pressure gave an oil (12 g.) which solidified when left in a desiccator. This product gave a positive test for chlorine and was hydrolysed by water to the original sulphinic acid.

The chloride (8·75 g.; 0·05 mol.) in benzene (50 c.c.) was added slowly with stirring to cold ethereal phenylmagnesium bromide (0·15 mol.). A solid was precipitated during mixing but this redissolved on continued stirring. The ether was replaced by benzene (200 c.c.) and the mixture refluxed for 18 hours. Decomposition with ice and ammonium chloride and fractionation of the benzene-soluble product gave diphenyl (0·6 g.), phenyl *p*-tolyl sulphide, b. p. 170—175°/18 mm., and phenyl *p*-tolyl sulphoxide, b. p. 200—210°/18 mm., m. p. 69—70°. Oxidation of the total sulphide and sulphoxide fractions in the usual manner gave 4·2 and 4·5 g., respectively, of phenyl *p*-tolyl sulphone, m. p. and mixed m. p. 124—125°.

Reaction between Phenylmagnesium Bromide and Thiophen-2-sulphonyl Chloride.—Thiophen-2-sulphonyl chloride (9·1 g.; 0·05 mol.) in benzene (75 c.c.) was added slowly with stirring to cold, ethereal phenylmagnesium bromide (0·15 mol). After replacement of the ether by benzene (75 c.c.) the mixture was refluxed for 22 hours and then decomposed with ice and ammonium chloride. The dried benzene extract yielded an oil which gave the following fractions: (i) b. p. 140—150°/20 mm., m. p. and mixed m. p. 70°, consisting of diphenyl (1·1 g.), (ii) b. p. 200—205°/20 mm. Fraction (ii) solidified when cooled, and crystallised from ligroin (b. p. 40—60°) in colourless plates (3·0 g.), m. p. 69° (Found: C, 70·9; H, 5·0; S, 17·3. Calc. for $C_{10}H_8OS_2$: C, 57·7; H, 3·8; S, 30·8%. Calc. for $C_{12}H_{10}OS$: C, 71·3; H, 5·0; S, 15·8%), which depressed the m. p. of phenyl 2-thienyl sulphoxide but not that of diphenyl sulphoxide.

Another experiment gave the compound, m. p. 69° (Found: C, 70·3; H, 5·0; S, 17·2%).

Oxidation of the above "sulphoxide" (3·0 g.) with 30% hydrogen peroxide (2 c.c.) in hot acetic acid (5 c.c.) gave, on cooling, the sulphone which crystallised from aqueous alcohol in colourless plates, m. p. 124° (2·9 g.) (Found: C, 61·6; H, 4·4; S, 19·1. Calc. for $C_{10}H_8O_2S_2$: C, 53·6; H, 3·6; S, 28·6%. Calc. for $C_{12}H_{10}O_2S_2$: C, 66·1; H, 4·6; S, 14·7%), unchanged by admixture with either phenyl 2-thienyl sulphone or diphenyl sulphone.

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The University, Leeds, 2. [*Received, May 9th,* 1947.]

NOTE.

The Action of Hydrogen Chloride on Isoprene. By A. J. Ultée.

Jones and Chorley (*J.*, 1946, 832) stated that " addition of hydrogen chloride to isoprene occurs in the 1 : 4-position ", but it is now found that the addition occurs primarily in the 1 : 2-position, the product being isomerised by the action of the hydrogen chloride. There is no doubt that, under the conditions used by those investigators, 1-chloro-3-methylbut-2-ene is the chief product, but other investigators have obtained different results. By reaction at 0° between hydrogen chloride and isoprene—probably less than an equivalent quantity—Bouchardat (*Compt. rend.*, 1879, **89**, 1117) obtained, besides unchanged isoprene, a product, three-quarters of which boiled between 86° and 91°, with no appreciable higher-boiling fraction. Aschan (*Ber.*, 1918, **51**, 1303), on the other hand, obtained a product of b. p. 107—110° (slight decomp.) and suggested that Bouchardat's result was due to the presence of 2-methylbut-2-ene in his isoprene, from which, Aschan believed, 2-chloro-2-methylbutane, b. p. 86°, had been formed. The objection to this supposition, however, is, not only that Bouchardat had so large a yield, but the far more important fact that his product was unsaturated, and that it added on two atoms of bromine to afford $C_5H_9ClBr_2$.

Claisen, Kremers, Roth, and Tietze (*J. pr. Chem.*, 1922, **105**, 76) obtained a mixture of a large quantity of primary hydrochloride and a small amount of the lower-boiling, 2-chloro-2-methylbut-3-ene : this means that both 1 : 4- and 1 : 2-addition took place.

By using only ¾ instead of 1 equiv. of hydrogen chloride, the author obtained an appreciable amount of this low-boiling compound : on fractionation under ordinary pressure unchanged isoprene is first obtained, followed by a fraction of b. p. 79—83° (50—55% of the theoretical amount calculated on the hydrogen chloride used) ; further distillation in a vacuum then afforded a 20% yield of the compound reported by Jones and Chorley.

Similar results were obtained both with the crude isoprene produced by pyrolysis of rubber (isoprene content, by maleic anhydride test, about 87%) and with isoprene purified through the sulphone.

According to Markovnikov's rule, there are four possible mono-addition products, *viz.*, 1-chloro-3- and -2-methylbut-2-ene (I and II, respectively), 3-chloro-2-methylbut-1-ene (III), and 2-*chloro*-2-*methylbut*-3-*ene* (IV), all except the last being known. Jones and Chorley's compound is (I) ; Tischtschenko (*Chem. Zentr.*, 1937, I, 572) has proved the structure of (II), b. p. 110°/760 mm. ; and according to Burgin, Engs, Croll, and Hearne (*Ind. Eng. Chem.*, 1939, **31**, 1413) (III) boils at 93·8°/760 mm. Hence only (IV) is left for the new compound, this being the only hydrochloride with a tertiary chlorine atom, which is compatible with the low b. p. Tischtschenko has commented on the easy transition from (III) to (II). In the same way, the new compound (IV) has a tendency to pass over into (I), for instance on boiling ; at low temperatures hydrogen chloride strongly accelerates the conversion, which would explain why Jones and Chorley did not isolate the compound, though it was potentially in their reaction mixture. By working under similar conditions, *i.e.*, by using 1 equiv. of hydrogen chloride, at least 5% of the low-boiling product could be obtained in addition to their main product.

By addition of bromine to (I) and (IV), two different compounds were obtained. Further details will be given later respecting a number of halogen compounds derived from (I) and (IV), but it may be stated here that 3 : 4-dichloro-2-methyl-but-1-ene, b. p. 63·5—64·5°/50 mm., results from chlorination of Jones and Chorley's compound with sulphuryl chloride in the presence of quinol, the former compound having been produced by other means by Petrov (*Bull. Soc. chim.*, 1946, 4D). This compound is identical with the dichloride of low b. p. which Jones and Williams (*J.*, 1934, 832) obtained when chlorinating isoprene : they mention only b. p. 60°/50 mm.

Hence 1 : 2-addition may also take place on chlorination, be it only as a minor side reaction.

Experimental.—Preparation. Dry hydrogen chloride was bubbled through isoprene, to which ether had been added (6 g. to 50 g. of isoprene) to increase the solubility of the hydrogen chloride. The tared glass bottle containing the isoprene was cooled in acetone–carbon dioxide, care being taken not to let the temperature of the contents rise above − 15°. After ¾ equiv. of the gas had been absorbed, the reaction mixture was set aside at low temperature overnight. It was neutralized with anhydrous potassium carbonate, dried with calcium chloride, and distilled at ordinary pressure, a little calcined potassium carbonate being placed in the distilling flask. After the unchanged isoprene and the ether had passed over, the temperature rose rapidly ; the fraction of b. p. 79—83° was collected separately and redistilled in a vacuum.

Properties. If 2-*chloro*-2-*methylbut*-3-*ene* (Found : Cl, 33·9, 34·1. C_5H_9Cl requires Cl, 33·9%) is kept at its b. p., the temperature of the liquid rises gradually. Under reduced pressure the compound can be distilled unchanged ; b. p. 79·5—80°/760 mm., 32°/120 mm., $d_2^{20°}$ 0·8855, $n_D^{20°}$ 1·4190 ; $[R_L]_D$ 29·81 (Calc. : 29·69). In the presence of hydrogen chloride, conversion into Jones and Chorley's compound takes place at low temperature : dry hydrogen chloride (0·5 g.) was passed into 2-chloro-2-methylbut-3-ene (10 g.) cooled in ice–salt, and after standing overnight the mixture was neutralized, dried, and distilled ; the main fraction had b. p. 111—113·3°, $d_{20°}^{20°}$ 0·9300, $n_D^{20°}$ 1·4480. Jones and Chorley give $d_4^{15°}$ 0·9380, $n_D^{20°}$ 1·4450.

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Some Aspects of the Chemistry of Hydrocarbons.

By C. N. HINSHELWOOD, M.A., Sc.D., D.Sc., F.R.S.

WHILE it may not be wholly unreasonable to fancy that to almost every element there falls some unique and perhaps indispensable rôle in the economy of Nature, it is also evident enough that some occupy the stage more conspicuously than others. The pre-eminence in structural chemistry which carbon owes to its electronic make-up and to its well-balanced position in the electrochemical scale involves almost of necessity the consequence that much of what might be called its functional chemistry is an affair of subtleties and half-tones. This certainly applies to the chemistry of hydrocarbons which at the first approach might have the air of a somewhat uninteresting group of substances but which on closer inspection reveal a rich variety of behaviour.

In the Presidential Address which I delivered last year I referred to the increasing importance of the interplay between the structural aspects and the kinetic aspects of chemistry. I propose now to consider from this point of view a few of the many problems presented by the hydrocarbons.

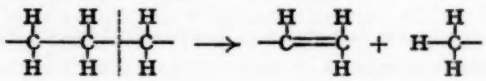
I shall first say something about what in some ways may be regarded as the most primitive of the reactions of hydrocarbons, namely their pyrolysis. We have known for some time that, under the usual conditions, the thermal decomposition is largely a chain reaction, its speed being reduced to a constant steady fraction of the original value by the addition of quite small amounts of nitric oxide to combine with free radicals. There is room for debate whether the residual reaction which occurs in presence of sufficient nitric oxide is itself a chain reaction of some sort, or whether it is a purely molecular change.

The arguments on the two sides may be briefly summarised as follows. Increasing amounts of nitric oxide reduce the rate of decomposition to a steady limit independent over wide ranges of further additions. This suggests a residual molecular reaction. The alternative is that there is a second kind of chain reaction with carriers unaffected by nitric oxide, or that a steady state is reached where the nitric oxide allows as many radicals to escape as it catches. One of several difficulties about this view is that in conditions where nitric oxide reduces the reaction rate of ethane to less than five per cent. it reduces that of various other paraffins only by about half, and yet the chain-propagating radicals to be assumed in the various cases would be closely similar. The fact that the products of inhibited and uninhibited reactions are nearly the same is not very good evidence either way, since radical mechanisms quite frequently work out to give overall products identical with those of a molecular reaction. One result which would be conveniently explained by the hypothesis of an unrepressed chain reaction is that the residual decomposition rate with excess of nitric oxide is roughly proportional to the power 1·5 of the hydrocarbon pressure. But this law is perhaps hardly established accurately enough or over a wide enough range to constitute unambiguous evidence, and it may simply be an approximate expression of the well-known transition from the first to the second order which unimolecular reactions can show.

I mention this matter as one which we must hope soon to clear up, but the main trend of my remarks will not be seriously affected by the answer. Let us take the example of *n*-hexane which has recently been re-studied by Partington and Danby in this laboratory. The products of the NO-inhibited decomposition are consistent with the occurrence of the series of reactions shown below. (Cf. Burk, Laskowski, and Lankelma, *J. Amer. Chem. Soc.*, 1941, **63**, 3248.)

$$\begin{aligned} CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 &\longrightarrow CH_4 + C_5H_{10} \\ &\quad\downarrow \\ &\quad C_2H_4 + C_3H_6 \\ &\longrightarrow C_2H_6 + C_4H_8 \\ &\quad\downarrow \\ &\quad 2C_2H_4 \\ &\longrightarrow C_2H_2 + C_2H_6 \end{aligned}$$

These are all molecular reactions of the type :



Auxiliary experiments showed that most of the pentene and a little of the butene would suffer a subsequent decomposition during the experiments, and on this basis the nature and proportion of products can be accounted for.

In the scheme represented above the two interesting matters are (*a*) the relative probabilities of rupture at the first, second, and third C–C links, (*b*) the question as to which end of the broken bond captures the hydrogen atom and which goes to form part of the double bond.

These two questions arise without fundamental change if a chain mechanism is assumed to apply even to the inhibited reaction. For at each fresh cycle of the chain a radical of some kind would have to remove a hydrogen atom from hexane giving one of the three following :

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{-}$$
$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CH_3$$
$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CH_2{\cdot}CH_3$$

Each of these would then have to split yielding an olefin and an alkyl radical (which would in turn yield the paraffin product by attacking fresh hexane). The problem of where the chain ruptures, and of the factors determining the capture of the H atom, remains. (In fact it should be remembered generally that many chain mechanisms involve as essential stages the decomposition of a complex radical, and that this process presents problems which are not essentially different from those met in the consideration of molecular reactions.)

On the basis of the scheme given for hexane, what is found is that (*a*) the probabilities of rupture are in the ratio :

C_{1-2}.	C_{2-3}.	C_{3-4}.
3·9	2·5	1

and (*b*) that the shorter carbon residue takes the hydrogen and becomes paraffin, while the longer furnishes the olefin.

The chance of the products

$$CH_3{\cdot}CH_2{\cdot}CH{:}CH_2 + C_2H_6$$

is more than ten times that of

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 + CH_3{\cdot}CH_2$$

The case of butane has been investigated by Steacie and Folkins (*Canadian J. Res.*, 1940, **18**, *B*, 1), the relative probability of C_{1-2} and C_{2-3} rupture being nearly equal.* Here the problem of the H-atom capture does not arise.

The interpretation of facts such as the above may involve considerations of two kinds, each of general interest and importance, namely the dynamics of carbon atom chains on the one hand, and the electronic properties of hydrocarbon systems on the other.

First we may ask what may be learnt from the modes of vibration of the carbon skeleton itself. According to the calculations of Pelzer (*Z. Elektrochem.*, 1933, **39**, 608; cf. also Slater, *Nature*, 1947, **160**, 576) on a classical system of n equal masses in a linear chain, the chance that a critical amplitude is reached in the relative displacement of two adjacent masses is the same for each position in the chain. The inference from this would be that the chances of C_{1-2}, C_{2-3}, and C_{3-4} ruptures would be equal. For butane this appears to be true of C_{1-2} and C_{2-3}, and for hexane the probabilities are, at least, of the same order of magnitude, though they are by no means precisely equal.

I have worked out the relative amplitudes for the three linear normal modes of *n*-butane and for the five corresponding modes of *n*-hexane, the results being as follows :

n-Butane.

	C_{1-2}.	C_{2-3}.	C_{3-4}.
Mode 1	0·50	0·70	0·50
2	0·70	0	0·70
3	0·50	0·70	0·50

* The probabilities of rupture are calculated from the proportions of products with correction for the fact that there are inherently two chances of C_{1-2} or C_{2-3} breaks to one of a C_{3-4} break with hexane, and two of a C_{1-2} break to each one of a C_{2-3} break with butane, *e.g.*, with butane the ratio $\frac{CH_4}{C_2H_6} = 1{\cdot}92$ and $\frac{C_2H_6}{C_2H_4} = 2{\cdot}04$, but allowing for the fact that C_{1-2} is equivalent to C_{3-4}, these must be divided by 2 to give the relative probabilities of rupture.

n-Hexane.

	C_{1-2}.	C_{2-3}.	C_{3-4}.	C_{4-5}.	C_{5-6}.
Mode 1	0·58	1	1·16	1	0·58
2	1	1	0	1	1
3	1·16	0	1·16	0	1·16
4	1	1	0	1	1
5	0·58	1	1·16	1	0·58

It is clear that sometimes the middle breaks will be favoured by the greater amplitudes of the displacements between the appropriate carbon atom pairs, and sometimes not. If all the modes are excited in collisions with equal ease there will be complete averaging, as Pelzer showed on the basis of the general Maxwell–Boltzmann equation. If we wish to explain a certain preference for C_{1-2} breaks with hexane and a relative infrequency of C_{3-4} breaks on a purely dynamical basis, we shall have to invoke more specific influences.

Mr. R. P. Bell has calculated the distribution of zero-point vibration amplitudes for various straight carbon chains and finds that the departure (Δ) of the link fron its equilibrium length is greater for terminal links than for others. The values of Δ^2 for the straight C_6 chain are 0·678, 0·645, and 0·640 respectively for C_{1-2}, C_{2-3}, and C_{3-4}. This factor would tend to operate in the required sense.

Another possibility is this : it might so happen that one or other of the modes which give no relative displacement of the C_3 and C_4 atoms is excited with special ease. I do not at present know of any special reason why this should happen, but I mention the matter specifically because it is one which might be susceptible to investigation by sound-dispersion measurements of the kind which led Alexander and Lambert to detect what may well be alternative modes of activation of acetaldehyde. It is hoped that this study may be extended to hydrocarbons with the object of finding out more about the excitation of the vibrations of the carbon skeleton.

Another line of attack which, however, seems to offer rather formidable difficulties is the further analysis of those parts of the infra-red spectrum which are associated with the skeleton vibrations of the carbon chain.

While we may hope for considerable advances in these directions it remains possible that for the group of facts which I have been discussing an electronic rather than an atomic explanation may be required.

The second question raised, namely which end of the ruptured chain takes the hydrogen atom, certainly seems to require interpretation in terms of electronic ideas. Perhaps, therefore, this may be a suitable opportunity to say something about this subject which is developing in a very interesting way at the present time.

Before discussing theoretical questions, I might remind you of one of two other phenomena which have probably to be discussed in similar terms. One is the tendency of longer alkyl radicals to break down into an olefin and a methyl group—a phenomenon of particular importance in the chain transfer process of polymerisation reactions. This type of process may become of such prominence that a long-chain polymer can, as Melville has shown, give a radical which sheds successive olefin molecules by the exact inverse of the polymerisation reaction by which it was formed.

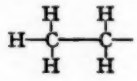
Older qualitative theories have had relevant things to say about the problem. For example, it has been customary in the past to speak of varying degrees of electronegativity of alkyl radicals and to suppose that radicals with relatively greater electron attraction would draw hydrogen from radicals with less. Again, alkyl groups are normally credited with the ability to repel electrons away from themselves to other parts of molecules, ethyl being more effective than methyl in this respect. Then again, various authors, including Werner and Flürscheim, have exploited the idea that in systems of the type A–X–B a strengthening of the bond X–A leads in general to a weakening of the bond X–B.

There are two important sets of general inferences from experimental facts that should also be relevant to the question. First, as judged from effects on the strengths of acids, alkyl groups repel electrons, and multiple carbon bonds attract them. Secondly, as judged from the force constants involved in the C–H vibrations in the infra-red spectrum of hydrocarbons, the tightness of binding of hydrogen to carbon decreases progressively in the structures :

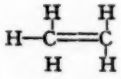
$$CH{:}CH;\ CH_2{:}CH_2 \text{ and } CH_4;\ CH_3{\cdot}CH_3;\ CH_3R,\ CH_2, \text{ and } CH.$$

Turning now to inquire what recent theory can offer in the way of general principles, we find an evolution of ideas, due to Mulliken, Wheland, Coulson, Walsh, and others, which aim at accounting for the subtler properties of the C–H and C–C bonds. For convenience I shall classify these ideas under headings, though they are to a considerable extent interrelated.

(1) The first development to which I shall refer is the notion that the bond of a hydrogen may be weakened, with corresponding strengthening of an adjacent C–C bond. In terms of the mathematical theory, which expresses the actual state of things as a superposition of other states which may not actually exist, it is said, for example, that the radical



partakes partly of the nature of



As Rice and Kossiakoff have pointed out, the possible alternative forms of the radical increase as one passes from a primary through a secondary to a tertiary alkyl radical of the same molecular weight. This by a well-known principle implies a greater stability and, probably, greater ease of formation of the branched radicals, and is not inconsistent with the fact that the binding of secondary and tertiary hydrogen atoms in hydrocarbons is weaker than that of primary carbon atoms. Rice and Kossiakoff see in this one of the principal factors governing the pyrolysis, but I am not clear how far it gives the answer to the two typical questions which I mentioned above in this connexion.

(2) Another important line of thought, closely related to the above, is that of the delocalisation of electrons in the bonds of saturated hydrocarbons. Delocalisation in unsaturated and conjugated systems is a well-defined phenomenon to which reference will be made later. In saturated systems it is a more subtle business, but probably lies at the basis of phenomena of great interest. It has been discussed especially by Coulson (*Quart. Reviews*, **1947, 1**, 144). The essential thing to note for our present purpose is that an electron of a C–H bond is not regarded as completely localised between the particular carbon and the particular hydrogen, and that the extent to which this electron is supposed to participate in other bonds is a function of the symmetry relations of the system. For example, the wave function for the three hydrogen atoms of CH_3, *regarded as a group*, is of the right symmetry to intereact with and to enter into delocalisation phenomena with the wave function associated with the fourth carbon bond. This effect is conveyed to some extent by the symbol $H_3{=}C{-}$, and is referred to as hyperconjugation. Coulson defines the condition necessary for delocalisation and stabilisation as the existence adjacent to a bond, but not actually part of it, of a group able to provide a molecular orbital of the right symmetry to combine with the electrons of the localised bond. It seems likely that the methyl group would play a special rôle in this respect in hydrocarbon chemistry, and indeed methyl groups do appear to exert influences of special kinds.

The binding of the hydrogen atoms in methane, as inferred from force constants, is greater than that in ethane : but the binding in ethane is greater than that of the hydrogen atoms in a CH_2 group of a longer paraffin. Furthermore, it is well known in various connexions that the electron-releasing character of the methyl group is specially great and reaches a very high intensity with the combined action of the three methyl groups of tertiary butyl. A further example of the peculiar influence of methyl groups will emerge presently. It is tempting to connect all these characteristics with the symmetry and the delocalisation phenomenon, though how far this idea will support quantitative testing is at present hard to say.

Returning for a moment to the problem raised above, the greater binding of the hydrogens in ethane as compared with those in CH_2 chains would provide a reason why the fragments formed by the incipient rupture of a C_6 chain should rearrange themselves to give

$$CH_3{\cdot}CH_3 + CH_2{:}CH{\cdot}CH_2{\cdot}CH_3$$

rather than

$$CH_2{:}CH_2 + CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3,$$

a greater combination of group orbitals being possible in the first case than in the second. Similar principles might indeed provide a partial explanation of why higher alkyl radicals should shed the symmetrical CH_3 group leaving an olefin of lower molecular weight (chain transfer in polymerisation reactions), and possibly even of the fact that, when a six-carbon chain breaks, $C_1 + C_5$ fragments are preferred to $C_3 + C_3$, C_1 having a great advantage in ease of delocalisation over C_3 but C_3 relatively little over C_5.

(3) The third respect in which theoretical ideas are developing is in connexion with the actual polarity of C–H bonds. In the C–H bonds of methane, Coulson argues from the nature

of the overall electron distribution that the carbon atom constitutes the positive end and the hydrogen atom the negative end of the dipole. The four electrons of tetrahedral carbon are hybridised from three p electrons and one s electron and have thus predominantly p character. Now it is considered that s electrons are more closely held than p electrons. Therefore, it is argued by Walsh that as carbon passes to states where its valencies possess more s character than in methane, so it should become more electronegative towards hydrogen. In ethylene the hydrogen atoms are held by bonds hybridised from s with only two p electrons and thus have in fact more s character: in acetylene this is still more so, since the H atoms are held by bonds hybridised from s and p. The result should be a reversal of the C–H dipole, with the carbon assuming the rôle of the negative end.

Here I may refer to the work of Bell and Thompson who have shown that, as far as the treatment of bending vibrations of substituted benzene derivatives is concerned, it is expedient to assume a negative carbon and a positive hydrogen.

I shall pass now to consider the oxidation of paraffin hydrocarbons, a subject in which very remarkable phenomena declare themselves.

It should first be mentioned that two fairly distinct types of reaction have to be distinguished, namely the so-called high-temperature and low-temperature mechanisms. The former governs the course of events with methane, the oxidation of which only occurs with appreciable speed at temperatures above 400°. It seems to depend upon chain reactions involving very primitive molecular fragments, such for example as the O atoms and CH_3 radicals postulated by Norrish for the case of methane itself. The low-temperature mechanism comes more and more into evidence as we pass from methane to butane, and with the higher hydrocarbons it is in operation at temperatures as low as 150°. The high-temperature mechanism provides a study in the resolution of reactions into their simplest steps, while the low-temperature mechanism illustrates some interesting subtleties of hydrocarbon chemistry.

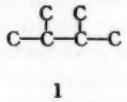
To summarise very briefly indeed the relevant kinetic facts, which have been fully treated elsewhere, we believe the reaction to be initiated by the removal of a hydrogen atom from the hydrocarbon by an oxygen molecule. The radical formed combines with more oxygen to give R–O–O– which attacks more hydrocarbon to give R–O–O–R′. The highly characteristic kinetics are due to the slow branching of reaction chains by the resolution of the peroxide into two radicals of the type R–O–. The rate of oxidation depends upon the initiation rate, ϕ, and upon the branching rate, μ, and the expression for the reaction velocity contains a factor of the form $\phi/(1 - c\mu)$ where c is a constant.

Structure of the hydrocarbon can influence both ϕ and μ, but the reaction rate is much more sensitive to the latter because the condition for rapid oxidation is precisely that $c\mu$ should approach unity. In these circumstances the term $1/(1 - c\mu)$ changes rapidly with change in μ itself. The oxidation rate, therefore, gives a magnified and sensitive measure of the influence of the structure of R on the stability of a peroxide of the type R–O–O–R or R–O–O–R′. It is chiefly on this subject that I am now going to speak.

The experimental results obtained during the last year or so by Mr. Cullis and Mr. Mulcahy show that the rate of oxidation increases with extraordinary rapidity with increase in the length of the chain in the normal paraffin series, the values relative to pentane being as follows:

Propane.	Butane.	Pentane.	Hexane.	Octane.	Decane
0·1	0·5	1	7·5	200	1380

The influence of branching in the chain is equally remarkable, as is shown by the following figures which refer to the relative oxidation rates of isomeric hexanes:



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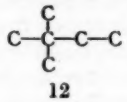

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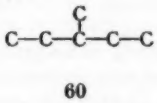

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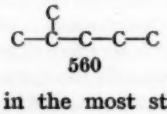

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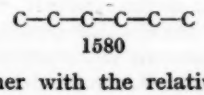

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These results contrast in the most striking manner with the relatively small influence of structure on the rate of pyrolysis.

In interpreting these two sets of results we have to bring under one heading two apparently rather diverse factors. Branching of the hydrocarbon chain and lengthening of it have opposite effects. Formally, this is accounted for if we attribute to the methyl group an influence

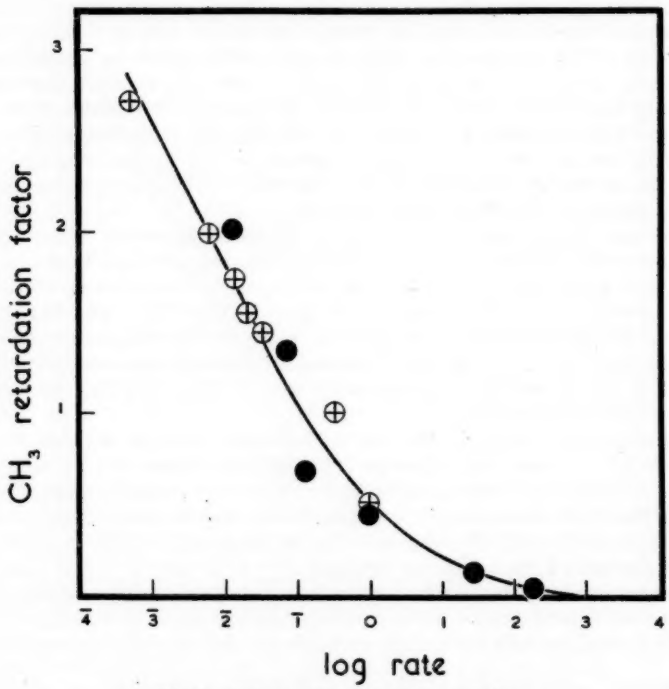
antagonistic to rapid oxidation, and if we further assume that its effect is damped (not enhanced) by intervening CH_2 groups. If, without inquiring further for the moment into its nature, we ascribe such an effect to the methyl group, then the results for the straight and the branched chain paraffins can be correlated.

Let us ascribe to the methyl group an antagonistic influence represented by 1·0 unit when it acts at an adjacent carbon atom, 1/3 when at a carbon atom one removed, and 1/9 when at an atom two removed. We further assume that the influences of all the methyl groups are additive. For example in

$$CH_3-\underset{}{\overset{CH_3}{CH}}-\overset{(1)}{CH_2}-\overset{(2)}{CH_2}-CH_3$$

the influence at (1) is $1/3 + 1/3 + 1/3 = 1{\cdot}0$
while that at (2) is $1 + 1/9 + 1/9 = 1{\cdot}22$.

In any given hydrocarbon it is easy to find at which carbon atom this resultant effect is *least* and to suppose that oxidation occurs at a rate which is some function of this factor.



Black circles; straight-chain paraffins.
Crossed circles; branched-chain paraffins.

The minimum values for various hydrocarbons are plotted in the Figure against the logarithms of the relative oxidation rates, the points referring to branched and unbranched hydrocarbons being distinctively marked. It is seen that both sets obey one functional relation, which seems to make out a prima facie case for the methyl group as the principal agent.

In the light of what was said above, it would seem that the determining factor is the stability of the peroxide R–O–O–X (where the bond R–O is formed at the point in the R chain least subject to the influence of the methyl). The natural conclusion is that the stability of the peroxide is increased by the electron-repelling tendency of the methyl group, a conclusion which I now prefer to the one provisionally entertained in a previous discussion. This matter needs a little further clarification. It is related to several other facts to which reference must first be made.

In the bimolecular hydrolysis of alkyl halides by hydroxyl ions, increasing chain length diminishes the rate of reaction (see A. G. Evans, " The Reactions of Organic Halides in Solution ", Manchester U.P., 1946). The usual explanation of this is that an *increased* electron-

repelling power of the *longer* alkyl groups causes greater resistance to the approach of the negative hydroxyl ion to the seat of reaction. This was the analogy which seemed at first sight to guide the interpretation of the results on chain length and oxidation rate. Such an interpretation, however, fails to deal at the same time with the straight and the branched chains, which can be satisfactorily treated in the way I have just mentioned, namely by assuming that intervening CH_2 groups *diminish* the effect of methyl. When one looks more carefully at the general question of the relative electron-repelling powers of longer and shorter alkyl groups it is seen not to be so clear-cut.

Some of the evidence may be summarised as follows :

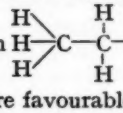
(1) Bond strength between carbon and halogen *decreases* and reaction rate with sodium *increases* with passage up the alkyl halide series. In view of this A. G. Evans attributes the diminishing rate of bimolecular hydrolysis to increasing steric hindrance.

(2) Dissociation constants of fatty acids show varied behaviour, but sometimes lengthening of the carbon chain *increases* the dissociation constant, that is, *diminishes* the electron release which would bind the proton more firmly. Thus, although K drops from acetic acid to propionic from $1{\cdot}86 \times 10^{-5}$ to $1{\cdot}4 \times 10^{-5}$, it rises again to $1{\cdot}48 \times 10^{-5}$ for butyric acid and to $1{\cdot}6 \times 10^{-5}$ for valeric acid.

(3) There is a striking contrast between the small and variable effects referred to under (1) and (2) and the very large effects due to the addition of extra methyl groups, especially of a trio of methyl groups in enhancing the electron release of tertiary butyl compounds.

It would seem in general that a CH_2 interposed between a methyl group and the seat of reaction may both contribute something of its own and damp the effect of the methyl.

The results on oxidation are best covered by the assumptions (*a*) that the peculiar kinetic mechanism brings the electronic effects into special prominence, (*b*) that the stability of the peroxides (in respect of splitting into radicals) is of major importance, (*c*) that the $-O-O-$ bond is *strengthened* by " electron accession ", (*d*) that methyl groups have a special potency in this respect and that their effect is *damped* by interposed CH_2 groups.

The hypothesis that the delocalisation effects in the group are of major importance in governing such electron-accession phenomena certainly raises interesting questions, including that of the reason why should be more effective than  . In a general way one can see that the symmetry relations in the former are more favourable than in the latter, but quantitative treatment of the problem would be useful.

The kinetic effects which are accounted for by the assumption that the methyl group has in fact this special potency are major ones, and to gather some of the threads together again I will summarise them. First, the remarkable reactivity of tertiary butyl compounds in halide hydrolysis reactions. Secondly, the enormous influence of the methyl substitution in the hydrocarbon oxidations. Thirdly, the vast preponderance, when the hexane chain breaks at the 2–3 position, of ethane and butene over ethylene and butane. Fourthly—though this is a less marked effect susceptible of other interpretations—the somewhat greater tendency for C_{1-2} breaks in the hydrocarbon chains. Fifthly, the great tendency for the shedding off of methyl radicals from longer alkyl radicals.

These matters bring me back to the general theme of hydrocarbon structure and reactivity, and to the fascinating field which it presents for the correlation of experiment, molecular dynamics, and valency theory.

Perhaps I may here mention the fact that some of my colleagues in this laboratory are at present studying the influence of substituents of various kinds, including unsaturated groups, on the oxidation and pyrolysis rates of hydrocarbons. I shall not anticipate their results, but mention simply that they raise in yet another form the immensely important question of the transmission of electronic influences along saturated carbon chains. The theoretical understanding of these transmission effects is of special importance, but also it would seem of special difficulty. They are subtle, but, as I said before, we believe that the study of oxidation rates in the gas phase brings them into special prominence.

I will now turn for a moment to a rather different question. Although many of the remarkable phenomena connected with the oxidation of hydrocarbons depend upon the character of the carbon atom, it is only right to observe that the nature of the reaction partner,

oxygen, is of hardly less moment. According to the hypothesis which I have discussed, the breaking of the O–O bond in R–O–O–R′ is one of the key processes. Now the ease and sensitiveness of this rupture is not unrelated to the fact that a single link between two oxygen atoms is very much weaker than half a double link. With sulphur the reverse is true, the single S–S link being more than half as strong as the double. It seemed, therefore, a matter of great interest to know whether the characteristics of the oxidation reactions would reveal themselves in the reactions between sulphur and hydrocarbons, and it was perhaps to be expected that they would not. Dr. Bryce has been examining some of the structural relationships. I shall not here anticipate the report which he will be making in due course about this matter, but I will just say that the effect of carbon chain length and structure so strikingly in evidence in oxidation appears to be absent in the sulphur reaction, and that, for example, hexane and dimethylbutane react about equally well with sulphur, although the ratio of the oxidation rates is of the order of a thousand.

As we have seen, certain quite general propositions about valency stand in a very direct relation to kinetic problems, and one naturally wonders how far we are on the road to a fundamental theoretical treatment of hydrocarbon stability and reactivity.

In some ways the application of valency theory to the chemistry of the saturated group is a little disappointing.

Problems such as that of the transmission of influences from one atom to another of a chain, or of the relation in a system X–A–Y between the respective strengths of the bonds A–X and A–Y, seem not yet to be amenable to any very illuminating treatment. On the other hand, marked success has attended the application of the theory to unsaturated systems, notably to quite complicated conjugated ring systems (see Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39; **192**, 16).

The reason for the distinction is in fact of some general interest. Conjugated systems are in the first place amenable to treatment by a special mathematical method. The σ electrons are allocated to the skeleton structure and assumed to retain their places. The π electrons are assigned to molecular orbitals, each described by a wave function which is taken to be expressible as a sum of atomic orbitals: $\phi = c_1\psi_1 + c_2\psi_2 + \ldots$, there being a separate ψ for each atom of the carbon skeleton. The total wave function of the molecule is the product of the wave functions for each π electron. The total density of π electrons on an atom j is given by Σc_j^2 and the order of the bond between atoms j and k by $\Sigma c_j c_k$, the sum being taken for each atom or pair of joined atoms over all the molecular orbitals. Application of the variation method gives a series of equations determing c_1, c_2 . . . and hence the electron densities and bond orders.

The results of the calculations depend upon two kinds of integral, α and β. It is customary in the treatment of series of molecules to take all α integrals involving carbon atoms only as equal to a standard value occurring in the calculation for benzene, and to use an empirical modification of this value for bonds C–X, where X is a hetero-atom in a ring system. The β integrals are put equal to zero for non-bonded atoms, and to a standard value for bonded atoms.

Now it is obvious that this procedure only introduces one element of specificity into the problem (apart from empirical changes in α for hetero-systems), and neglects the sort of factors which would be of great importance in determining the finer details of behaviour for saturated hydrocarbons. The specific factor governing the result is simply the number of neighbours which each successive carbon atom of the skeleton possesses. The calculation achieves great success in accounting for the properties of conjugated carbon ring systems of various shapes and sizes, and, with a single empirical parameter in a given case, for the characteristics of hetero-systems.

It would appear, therefore, that much of the elaborate chemistry of the great class of conjugated hydrocarbon ring systems is essentially a function of geometry alone, and can be understood in broad outline without solving the problem of subtler influences. It is, I think, not without interest that Nature should work in this way.

The factors which would determine second-order effects in the conjugated systems become the most important differences in the saturated systems, and since they remain small they reveal themselves only to experimentation of a subtler kind. Such experimentation must continue, and, it is to be hoped, the mutual interaction between it and the further developing theory will be to the benefit of both.

ONE HUNDRED AND SEVENTH ANNUAL GENERAL MEETING.

THE One Hundred and Seventh Annual General Meeting of The Chemical Society was held in the Lecture Theatre of the Physical Chemistry Laboratory, South Parks Road, Oxford, at 12 noon on Thursday, March 18th, 1948. The President, Professor C. N. Hinshelwood, was in the chair.

The notice convening the meeting was read.

In presenting the Report of Council for 1947, copies of which were available, Professor Wardlaw referred in particular to the Centenary Celebrations, an event in the history of the Society which had met with outstanding success. The continued success of the Society was reflected in its steady progress, the high reputation of its publications, and the progressive growth of the Fellowship.

The Publication Committee was dealing with energy and foresight with the difficulties imposed by the shortage of paper, and steps were being taken which would, it was hoped, reduce the delay in publication. The *Quarterly Reviews* had met with immediate success, and the two volumes—" The Chemical Society, 1841—1941 " and " British Chemists "—published in connection with the Centenary were recognised to be of outstanding merit.

Professor Wardlaw referred also to the increase in the number of meetings of the Society held outside London during the past year as a sure indication of the expansion of the Society's influence. In conclusion, he referred briefly to the other activities of the Society, to the number of grants made from the Research Fund, and to improvements made in the heating and lighting of the Library.

In reply to a Fellow, the President stated that the Board of Trade had now agreed to supply in full the current paper requirements for the *Journal*, and that, provided the printers were able to maintain an increased output, the delay in the publication of scientific communications should now be gradually reduced.

In proposing the adoption of the report of Council, Dr. J. D. Loudon referred to the understanding which the Officers and Council had always shown towards the problems of Local Representatives. The proposal was seconded by Dr. W. Rogie Angus, and the Report was adopted.

The following elections to vacancies on Council were announced :—

President :

Sir Ian Heilbron.

Treasurer :

Sir Wallace Akers.

Honorary Secretary :

Dr. Alexander King.

Elected Ordinary Members of Council :

Constituency II :

Dr. L. L. Bircumshaw.
Dr. T. Malkin.
Dr. S. Peat.

Constituency III :

Dr. A. E. Gillam.

Constituency V :

Professor F. S. Spring.

Constituency VI :

Professor T. S. Wheeler.

It was announced that as no valid nomination had been received to fill the vacancy for Constituency IV (North-East England), Council had nominated Professor G. R. Clemo to fill this vacancy.

The report of the Scrutators on the ballot for Vice-Presidents who have not filled the Office of President, and for Elected Ordinary Members of Council for Constituency I, had been received, and it was declared that the following had been elected :—

Vice-Presidents who have not filled the Office of President :

Mr. R. P. Bell.
Dr. G. M. Bennett.
Professor A. R. Todd.

Elected Ordinary Members of Council :

Constituency I :

Dr. A. H. Cook.
Dr. L. E. Sutton.

It was proposed by Dr. W. B. Whalley, and seconded by Professor F. E. King, that Messrs. W. B. Keen & Co. be appointed to audit the accounts for 1948. This was carried.

A vote of thanks to the President, Officers, and Council was proposed by Professor T. S. Wheeler. He referred especially to the retiring Officers and Members of Council, and paid tribute to the efficient service they had freely given for the benefit of the Society. The vote of thanks was seconded by Dr. D. O. Jordan and carried with acclamation.

In his reply, the President referred to the pleasure he had gained from his association with the administration of the Society during his period of office, and expressed the Council's warm appreciation of the work of the permanent staff of the Society.

The Anniversary Luncheon was held in Oriel College at 1.15 p.m. The toast of " The Chemical Society " was proposed by the Vice-Chancellor, Dr. W. T. S. Stallybrass. He referred to the many associations of the University of Oxford with chemistry and with the Chemical Society, and expressed his pleasure at being able to welcome the Society to Oxford. In reply, the President stated that while the Centenary Celebrations had been an unqualified success and of very great value in giving expression to the corporate existence of the Society, it was by its everyday activities that the Society would ultimately be judged.

At a well-attended afternoon meeting, the Harrison Memorial Prize for 1947 was presented to Dr. D. H. R. Barton. The President then delivered his Presidential Address entitled " Some Aspects of the Chemistry of Hydrocarbons." At the conclusion, a vote of thanks to the President for his Address, and a request that he would allow the address to be printed in the *Journal* was proposed by Sir Norman Haworth, seconded by Lady Robinson, and carried with acclamation.

The new President, Sir Ian Heilbron, was then formally installed in office. Sir Ian expressed his great pleasure at the honour the Society had bestowed on him by electing him to be its President. He referred briefly to the tasks facing the Society and in particular to the need of accommodation befitting its dignity.

Later in the afternoon, Fellows of the Society and their friends were the guests of the Vice-Chancellor at a reception in Christ Church, and in his unavoidable absence the guests were received by the Master of Pembroke, The Rev. F. H. Dudden.

REPORT OF COUNCIL FOR 1947.

I. CENTENARY CELEBRATIONS.

The Chemical Society celebrated in London on July 15th—17th the Centenary of its foundation. Delegates representing the learned societies of twenty-eight nations journeyed to London to present Addresses of Congratulation and to participate, together with over fourteen hundred Fellows of the Society, in these Celebrations. Learned Societies in Great Britain also paid tribute to the achievements of the Society.

The following message signed by His Majesty The King was received and read at the Opening Ceremony :

> " I sincerely thank you, the Council and Fellows of the Chemical Society, for your kind and loyal message.
>
> As your Patron, I deeply appreciate the contribution which your Society has made and continues to make to the common good, and on the occasion of your Centenary I send my best wishes to all those who are taking part in the celebrations.
>
> GEORGE R.I."

The University of London conferred Honorary Degrees of Doctor of Science on the President and on three Honorary Fellows of the Society, Professors Brønsted, Karrer, and Pauling.

The Society was honoured by the presence of the Prime Minister The Rt. Hon. C. R. Attlee and Mrs. Attlee, as the principal guests at the Centenary Dinner.

Joint Meeting with the Royal Society of Arts. A Special Joint Meeting was held at the Royal Society of Arts on February 19th, 1947, to commemorate the formation of the Society on February 23rd, 1841. Sir Harold Hartley delivered his lecture, " A Century of Chemistry ", before a large audience.

The Centenary Exhibition. A historical exhibition organised by Sir Robert Robertson and designed to illustrate the advances made by British Chemists during the past hundred years was held at the Science Museum from July 14th to September 30th. A Section arranged by the Department of Scientific and Industrial Research illustrated the place of Chemistry in the daily life of the community.

The catalogue of this exhibition, " Chemical Progress ", was prepared by authorities in each branch of Chemistry. More than four thousand copies were sold.

Programme. The principal events in the programme were as follows :

Monday, 14th July.

11.00 a.m. Opening of the Centenary Exhibition.

Tuesday, 15th July.

9.45 a.m. Reception of delegates.
11.00 a.m. Opening Ceremony of the Celebrations.
1.00 p.m. Luncheons given by H.M. Government and by the Ladies Committee.
3.30 p.m. The Centenary Address by the President.
7.30 p.m. The Centenary Dinner.
8.00 p.m. Reception and dance.

Wednesday, 16th July.

9.00 a.m. Visits to laboratories.
11.00 a.m. Lectures : (i) by Professor J. Read, M.A., Sc.D., F.R.S.; (ii) by Professor E. K. Rideal, M.B.E., M.A., D.Sc., F.R.S.
3.00 p.m. The Faraday Lecture by Sir Robert Robinson, M.A., D.Sc., LL.D., P.R.S.
6.00 p.m. Graduation Ceremony and Dinner by the University of London.
8.30 p.m. Reception by Imperial Chemical Industries Ltd.

Thursday, 17th July.

9.00 a.m. Visits to laboratories.
4.00 p.m. Garden party given by H.M. Government.
6.00 p.m. Reception by the Royal Institution.
8.30 p.m. Reception by the Royal Society.

Acknowledgments. The Council desires to record its grateful appreciation and thanks to those who assisted in the preparations for the Celebrations, and to those bodies that provided hospitality and entertainment to Fellows of the Society and their guests.

Centenary Expenses Fund. The Council record their thanks to the Guarantors to the Centenary Expenses Fund whose names appear in the *Proceedings* for January, 1948.

The Centenary Expenses Fund has now been closed and the consolidated account appears in the Annual Financial Statement.

Centenary Fund. The Council is gratified to record the generous support received from industrial and other organisations, and from Fellows. The total contributions promised amounted to £31,454 at December 31st, 1947. The list of contributors appears in the *Proceedings* for January, 1948.

Report of the Centenary Proceedings. A report of the main events of the Celebrations is in preparation and will be published in 1948.

II. FELLOWSHIP.

1. *Honorary Fellowship.* On March 6th, Professor John H. Northrop and Professor Tadeus Reichstein were elected Honorary Fellows of the Society.

2. *Fellowship Statistics.* During 1947, 929 Fellows were elected and 23 reinstated, the corresponding figures in 1946 being 732 and 29 respectively. The Society has lost 48 Fellows by death, 194 by resignation, and 130 by removal, making a total loss of 372 as against 145 in 1946. The number of Fellows on December 31st, 1947, was 7485. Of these 3249 were joint members of the three Chartered Bodies and 1184 were joint members of the Chemical Society and the Society of Chemical Industry alone. Of those who became joint members of the three bodies in 1947, 245 are new Fellows of the Chemical Society, and, of those who became joint two-body members 187 are new Fellows. The number of joint members of the three bodies has increased during the year by 163, the number of joint members of the two bodies by 133, and the number of single-body Fellows has increased by 269.

3. *Joint Student Facilities.* During 1947, 29 persons have been granted joint student facilities by the two publishing societies under the Chemical Council scheme.

4. *Honours.* The congratulations of the Society were conveyed to the following Fellows who received during the year the honours indicated:

Professor W. N. Haworth, Knight Bachelor.
Professor E. L. Kennaway, Knight Bachelor.
Professor J. A. Prescott, C.B.E.
Dr. E. W. Smith, Knight Bachelor.
Professor T. Wallace, C.B.E.

The Council also conveyed congratulations to Sir Robert Robinson on the award of the Nobel Prize for Chemistry for 1947, and to the following Fellows who have been awarded medals by the Royal Society:

Professor C. N. Hinshelwood, Royal Medal.
Professor F. Joliot, Hughes Medal.
Professor L. C. Pauling, Davy Medal.

5. *Special Concession to University Students who have served in H.M. Forces.* At its meeting on January 9th, the Council agreed that, from January 1st, 1947, those who have served in H.M. Forces can be Fellows paying a reduced subscription or participate in the joint junior subscription scheme until they have obtained their first University degree.

6. *Deaths.* The Council learned with profound regret of the death of two distinguished Honorary Fellows of the Society, Professor V. M. Goldschmidt, and Sir Frederick Gowland Hopkins (Vice-President 1921—1924).

By the death, on March 10th, of Dr. Alexander Scott, the Society lost one of its senior Fellows. Dr. Scott was a Fellow of the Society for sixty-eight years and was first elected a member of Council in 1897. He became Honorary Secretary in 1899, Treasurer in 1904, and President in 1915. Following his Presidency, Dr. Scott continued to serve the Society as Vice-President (1917—1928 and 1930—1933).

The Council also heard with sorrow of the death of Professor J. M. Gulland who had served the Society as Honorary Secretary (1933—1936) and as a member of Council (1941—1944).

III. PUBLICATIONS.

1. *Journal.* During the year, 523 scientific communications were received, of which 9 were declined and 3 were withdrawn. The *Journal* which, having regard to the smaller type at present in use, was as large as, if not larger than, any previously published by the Society, comprised 396 items made up as follows:

Papers (General, Physical, and Inorganic, including 7 papers of a Discussion on Macromolecules)	67
,, (Organic)	279
Notes	29
Lectures and Addresses	9
Obituary Notices	8
Annual General Meeting	2
Reports on Atomic Weights	2

Scientific communications published during the year included contributions from India (4), Canada (1), Australia (9), New Zealand (7), Ceylon (1), Palestine (3), Egypt (9), and France (2).

The following figures show the growth of publication during recent years, and the increasing task facing the Society:

	1944.	1945.	1946.	1947.
Scientific communications received	242	347	453	523
Published	199	262	278	375
Journal, pages	679	930	1175	1709

2. *Annual Reports.* Owing to the fuel crisis affecting the printing trade, and other causes, the *Annual Reports* for 1946 were again regrettably late: they were, however, available to subscribers some five months earlier than the *Annual Reports* in the previous year, and it is hoped to publish the *Annual Reports* for 1947 nearer to the normal pre-war time.

3. *Quarterly Reviews.* The year marked the launching of this new enterprise. The first volume of the *Quarterly Reviews* occupied 395 pages, and contained 14 articles, varying in length from 13 to 67 pages, on selected topics from the fields of general and physical, inorganic, and organic chemistry.

4. *Centenary Volumes.* In connection with the Centenary Celebrations of the Society two volumes were published: "The Chemical Society, 1841—1941", a historical review, by T. S. Moore and J. C. Philip, and "British Chemists", edited by A. Findlay and W. H. Mills. The cost of these volumes was generously defrayed by Messrs. Richard Clay and Company, Ltd., as a contribution to the Centenary Fund.

IV. MEETINGS.

1. *Scientific Meetings.* The Society has held 19 Meetings in London during 1947. These included 10 lectures and 2 organised discussions. At the other 7 meetings 18 papers were read and discussed.

The number of meetings held outside London increased from 65 to 77. These included 69 lectures, 6 meetings for reading papers, 1 discussion, 1 scientific film display, and 1 demonstration of scientific apparatus. Of these meetings 56 were held jointly with local sections of other bodies or with University Chemical Societies.

An Official Scientific Meeting of the Society was held at Bristol on February 13th, 1947.

A complete list of meetings is given in Appendix B.

2. *Anniversary Meeting.* A report of the Anniversary Meeting held in London on March 20th appeared in the *Journal* for May.

The Meeting consisted of the 106th Annual General Meeting and Presidential Address; the Anniversary Luncheon was held at the Dorchester Hotel, and in the evening a party of Fellows and their friends attended a performance of Ben Jonson's " The Alchemist ".

The Annual General Meeting was adjourned until June 5th when the accounts for 1946 were presented and auditors appointed; these accounts were published in the *Journal* for June, 1947.

V. LIBRARY.

The Annual Report of the Joint Library Committee for 1947 appears as Appendix A.

VI. OTHER ACTIVITIES.

1. *Grants for Research.* During the year the Council authorised the payment of research grants amounting to £385 to 17 applicants.

2. *International Union of Chemistry.* The Council entertained the Council and Bureau of the International Union of Chemistry to Luncheon on July 23rd, 1947.

3. *International Exhibition, 1951.* Professor W. Wardlaw represented the Society at a preliminary conference, called by the Royal Society of Arts, to consider the proposal for an International Exhibition in 1951.

VII. ADMINISTRATION.

1. *Personnel of Council.* At the Annual General Meeting on March 20th, the following elections were made :

Vice-President	Dr. J. Kenyon.
Ordinary Members of Council	Dr. G. M. Dyson, Dr. F. R. Goss, Dr. F. M. Hamer, Dr. F. E. King, Dr. H. N. Rydon.

2. *Local Representatives.* In February the Council appointed Professor Brynmor Jones to be the Society's first Local Representative in the Hull area.

The resignation of Dr. A. E. Gillam as Local Representative in Manchester was accepted with regret. The Council appointed Dr. G. Baddeley to fill the vacancy.

3. *General Secretary.* Mr. J. R. Ruck Keene was appointed General Secretary on November 1st, 1947, in succession to Mr. L. R. Batten who resigned from the position in order to take up a business appointment.

VIII. FINANCE.

1. *Investments.* The following alterations in the Society's investments have been made during the year :

£330 standing to the credit of Life Composition Fees in General Purposes Account, invested in 2½% Treasury Stock, 1975 or after.

£750 standing to the credit of Life Composition Fees in General Purposes Account, invested in 2½% Savings Bonds 1964—1967.

£3825 1*s.* 6*d.* 3% Local Loans on General Purposes Account converted into 2½% Treasury Stock 1975, or after.

£4741 4*s.* 10*d.* 3% Local Loans on Research Fund Account converted into 2½% Treasury Stock 1975, or after.

£3344 3*s.* 4*d.* 3% Local Loans on Publications Fund Account converted into 2½% Treasury Stock, 1975, or after.

£1520 14*s.* 3*d.* Cardiff Corporation 3% Redeemable Stock 1914—1954 on General Purposes Account converted into 2¾% Cardiff Corporation Redeemable Stock 1966—1971.

£5000 on Centenary Fund Account invested in 2½% Savings Bonds 1964—1967.

£4000 on Centenary Fund Account invested in 3% Savings Bonds 1955—1965.

£898 19*s.* 6*d.* on the Society's Australian Account (General Purposes Account) invested in 4% Commonwealth of Australia Treasury Bonds 1961.

£391 17*s.* 4*d.* 3% Local Loans on Staff Pensions Fund was redeemed and not re-invested.

Authority was given for the redemption of £800 3% Defence Bonds on Special Reserve Fund.

2. *Emile Mond Bequest.* The Emile Mond Bequest of £100 has been transferred from the Special Reserve Fund to the Centenary Fund.

3. *Increased Prices of Publications.* Rising costs of printing, paper, and the generally increased cost of all administrative services have made it necessary to revise the arrangements for the supply of publications under the Basic Subscription.

As from January 1st, 1948, Fellows paying a subscription of £3 10*s.* will receive publications to the value of £3 without further charge, and may make additional purchases over and above this amount at the reduced rate to Fellows. Fellows paying a reduced subscription of £1 15*s.* will receive publications to the value of £1 10*s.* without further charge, and may make additional purchases at the reduced rate up to a further £1 15*s.*

The Council feel that the adoption of this new method of choice for separate Fellows is the most equitable arrangement since the extra amount which they will be called upon to pay will be in proportion to the number of publications they desire to receive.

The new prices of publications also apply to Fellows paying Joint Subscriptions.

4. *Insurances.* Fire insurances on the Library, and on stocks of publications and paper, have been increased by appropriate amounts.

5. *Contributions.* The Council records with thanks the following contributions towards the cost of publications:

£750 on account of 1946, and £1000 on account of 1947, from the Chemical Council.

£900 from the Government Grant distributed by the Royal Society.

The Anglo-Iranian Oil Co., Ltd., has entered into a Deed of Covenant to pay the Society a sum of £50 per annum for seven years to be used for the current general purposes of the Society.

6. *Library.* Contributions have been received through the Chemical Council towards the maintenance of the Library for 1946, from:

	£	*s.*	*d.*
The Royal Institute of Chemistry	962	17	7
The Society of Chemical Industry	516	16	0
The Faraday Society	108	16	0
The Society of Public Analysts and Other Analytical Chemists	87	0	10
The Chemical Council	900	8	6

Contributions have been received from other sources as follows:

	£	*s.*	*d.*
The Association of British Chemical Manufacturers	100	0	0
The Biochemical Society	21	0	0
The British Association of Chemists	50	0	0
The Institute of Brewing	50	0	0
The Society of Dyers & Colourists	10	10	0
Genatosan, Ltd. (under Deed of Covenant)	25	0	0

7. *Special Reserve Fund.* £300 has been transferred to the Special Reserve Fund towards expenses of the Quinquennial Index of *British Abstracts.*

IX. RELATIONS WITH OTHER BODIES.

(1) *Representatives of the Society on other Bodies.*

During 1947 the Society was represented as follows:

Anglo-Soviet Scientific Collaboration Sub-Committee:

Sir John Russell.

Association of British Chemical Manufacturers:

Joint Technical Committee on Patents: Dr. J. T. Hewitt.

Barker Committee:

Formed to support the publication of the Barker Index of the characteristic angles of crystalline compounds: Dr. G. M. Bennett.

Bristol University Court:

Professor F. G. Donnan.

British National Committee for Chemistry:

Sir Norman Haworth, Sir Ian Heilbron, Dr. W. H. Mills.

British National Committee for Crystallography:

Dr. G. M. Bennett.

British Standards Institution. Technical Committees:

Co-ordinating the work of the Divisional Councils in regard to any British Standard which may be issued in future for units, conversion factors, fundamental formulæ, values for properties of materials, etc.: Professor S. Sugden.
Standardisation of microchemical apparatus: Professor H. V. A. Briscoe, Dr. H. D. K. Drew.
Specifications for Materials and Plant used in Electroplating: Dr. U. R. Evans.
Standardisation of Scientific Glassware: Dr. G. R. Davies.
Standards for use in Dairying Chemistry: Mr. Eric Voelcker.
Standardisation of Letter Symbols: Professor S. Sugden.
Technical Committee C/17 Viscosity: Dr. A. E. Dunstan.

Bureau of Abstracts.

Directors and Members: Dr. G. M. Bennett, Mr. F. P. Dunn, Dr. E. B. Hughes, Dr. E. H. Rodd.
Members: Mr. R. P. Bell, Professor H. V. A. Briscoe, Dr. A. H. Cook, Professor W. Wardlaw.

Chemical Council:

Dr. R. P. Linstead, Professor C. N. Hinshelwood, Professor W. Wardlaw, Mr. F. P. Dunn.

Chemical Council—Advisory Committee on the Dyson System of Ciphering Chemical Compounds:

Professor Wilson Baker, Dr. E. H. Rodd, Professor A. R. Todd.

City and Guilds of London Institute:

Professor H. V. A. Briscoe.

Faraday Society—Colloid Committee:

Dr. G. S. Hartley.

International Union of Chemistry:

Committee for the Reform of the Nomenclature of Organic Chemistry: Professor C. S. Gibson.

Joint Library Committee:

Professor H. Bassett, Dr. O. L. Brady, Dr. C. H. Desch, Mr. M. B. Donald, Mr. F. P. Dunn, Professor H. J. Emeléus, Dr. P. Haas, Dr. T. A. Henry, Dr. J. I. R. Hepburn, Professor D. H. Hey, Dr. Harold King, Professor G. A. R. Kon, Professor E. E. Turner, Professor W. Wardlaw.

Lawes Agricultural Trust:

Committee of Management: Sir Norman Haworth.

Parliamentary and Scientific Committee:

Professor C. N. Hinshelwood, Professor D. H. Hey.

Royal Society.

Joint Standing Committee for Symbols and Abbreviations: Professor C. W. Davies, Professor S. Sugden.

Safeguarding of Industries Committee:

Professor C. S. Gibson.

Yorkshire Council for Further Education:

Advisory Committee for Chemistry in South and East Yorkshire: Professor R. D. Haworth, Professor Brynmor Jones.

APPENDIX A.

ANNUAL REPORT OF THE JOINT LIBRARY COMMITTEE FOR 1947.

Figures for all departments of the work of the Library during the year again show an increase. This is most marked in the case of photostat copying, 5040 printed pages having been copied, as against 4174 in the previous year. Attendances by readers rose by 340 and books borrowed by 130. Telephone enquiries dealt with amounted to 1711, an increase of 151 on last year.

The number of books added to the Library totalled 442, of which 157 were presented. 617 volumes of periodicals and 143 pamphlets were added. The number of volumes in the Library is now 48,922, of which 14,772 are books and 34,150 volumes of periodicals.

Analysis.

	Attendances.	Books borrowed.	Books added.	Volumes of periodicals.	Pamphlets.
1947	11,710	9678 (3427 by post)	442	617	143
1946	11,370	9548 (3396 by post)	254	593	181

An interesting commentary on the way in which the use of the Library has increased is provided by the figures for the year 1920, the first full year in which the scheme of co-operation operated. In that year the attendances numbered 4716 and the books borrowed 3079, which is fewer than the number now borrowed by post alone. The large increase in the number of books added is accounted for by the inclusion of books purchased in Germany.

The heating of the Library has been considerably improved by the replacement of the open fireplaces by slow combustion stoves.

Several experts have visited the Library to see the fluorescent lighting. They describe the casing as a very fine example of "Perspex" work. Photographs of the Library, illuminated by this lighting, have been taken for use at an international lighting conference.

Many visitors to the Centenary Celebrations and the International Congress took the opportunity of visiting the Library, and an exhibition of some of the Society's early historical books aroused much interest.

Gifts in connection with the Centenary were five early historical books presented by the Iron and Steel Institute, and a palladium–hydrogenium medal struck by Thomas Graham when he was Master of the Mint, presented by Mr. T. H. Russell. A noteworthy bequest was a set of the complete works of Robert Boyle in six volumes, from the late Dr. Alexander Scott, F.R.S. The Committee desires to express its thanks to all those who presented books to the Library.

The pressing need for a reading room worthy of the Society's unique collection of chemical literature becomes ever more obvious. Every fresh attempt to provide more seating to meet the increased demand leads to a further dispersal of books, and this in turn makes it increasingly difficult to meet the requirements of readers with that promptitude which they have learned to expect.

APPENDIX B.

MEETINGS HELD DURING 1947.

IN LONDON.

Unless otherwise stated all meetings were held in the Rooms of the Society at Burlington House.

January 9th, *Meeting* for reading papers; February 6th, *Tilden Lecture*, "The Application of Surface Chemistry to Colloidal Problems", by Dr. A. E. Alexander; February 19th, Special Commemorative Meeting with the Royal Society of Arts, *Lecture*, "A Century of Chemistry", by Sir Harold Hartley; February 20th, *Meeting* for reading papers; March 6th, *Meeting* for reading papers; April 17th, *Discussion* on "Electrolytic Solutions", arranged by Professor C. W. Davies; May 1st, *Meeting* for reading papers. June 5th, *Meeting* for reading papers; July 15th, at the Central Hall, Westminster, "The Centenary Address", by Professor C. N. Hinshelwood; July 16th, at the Institution of Civil Engineers, *Lecture*, "Chemical Personalities a Century Ago", by Professor J. Read; July 16th, at the Royal Institution, *Lecture*, "The Work of the Royal Institution in Physical Chemistry in Great Britain", by Professor E. K. Rideal; July 16th, at the Central Hall, Westminster, *Eighteenth Faraday Lecture*, "The Development of Electrochemical Theories of the Course of Reactions of Carbon Compounds", by Sir Robert Robinson; October 2nd, *Ernst Julius Cohen Memorial Lecture*, by Professor F. G. Donnan; October 23rd, *Tilden Lecture*, "Crystallographic Technique and its Chemical Significance", by Professor E. G. Cox; November 6th, *Meeting* for reading papers; November 20th, *Meeting* for reading papers; December 4th, *Pedler Lecture*, "Recent Developments in the Vitamin-A Field", by Sir Ian Heilbron; December 17th, at the Royal Institution, *Lecture*, "Chemical Personalities a Century Ago", by Professor J. Read; December 18th, *Discussion* on "Infra-red Spectra and Molecular Structure", introduced by Dr. H. W. Thompson.

OUTSIDE LONDON.

Aberdeen. At Marischal College. January 24th, *Lecture*, "Recent Advances in our Knowledge of the Metabolism of Proteins and Amino-acids", by Dr. D. P. Cuthbertson;

February 28th (joint meeting with the local sections of the Royal Institute of Chemistry and the Society of Chemical Industry), *Lecture*, "Grinding and Size Reduction: Some Problems met in the Fertiliser Industry", by Mr. R. H. Calvert; March 11th, *Lecture*, "The Composition and Structure of Proteins", by Professor A. C. Chibnall; March 20th (joint meeting with the local sections of the Royal Institute of Chemistry and the Society of Chemical Industry), *Lecture*, "Recent Developments in the Chemistry of Starch and Glycogen", by Professor E. L. Hirst; October 24th (joint meeting with the local sections of the Royal Institute of Chemistry and the Society of Chemical Industry), *Lecture*, "New Methods in Applied Organic Analysis", by Mr. R. Belcher; November 14th (joint meeting with the local sections of the Royal Institute of Chemistry and the Society of Chemical Industry), *Lecture*, "Recent Developments in Synthetic Fibres", by Dr. D. Traill; December 12th (joint meeting with the local sections of the Royal Institute of Chemistry and the Society of Chemical Industry), *Lecture*, "Bond-length Variations in Aromatic Systems", by Professor J. M. Robertson.

Birmingham. At the University: February 21st (joint meeting with the University Chemical Society), *Lecture*, "Surface Chemistry and Colloids", by Dr. A. E. Alexander; May 5th, *Lecture*, "Careers in Chemistry", by Mr. M. C. Paine; December 8th (joint meeting with the University Chemical Society), *Lecture*, "Mechanisms of Oxidation", by Dr. W. A. Waters.

Bristol. At the University: February 13th, Official Meeting of the Society, *Discussion* on "Protein Chemistry", opened by Professor J. D. Bernal; November 6th (joint meeting with the local sections of the Royal Institute of Chemistry, the Society of Chemical Industry, and the University Chemical Society), *Lecture*, "The Oxidation of Phenols", by Professor R. D. Haworth.

Cambridge. At the University: January 17th, *Tilden Lecture*, "Macromolecules Synthesised by Micro-organisms", by Professor M. Stacey; November 7th (joint meeting with Cambridge University Chemical Society), *Lecture*, "A Problem in Chemical Kinetics", by Professor C. N. Hinshelwood.

Edinburgh. At the North British Station Hotel (joint meetings with the local sections of the Royal Institute of Chemistry and the Society of Chemical Industry): February 20th, *Lecture*, "Fluorescence", by Dr. N. Campbell; March 13th, *Lecture*, "The Composition and Structure of Proteins", by Professor A. C. Chibnall; October 16th, *Lecture*, "Modern Ideas of Valency", by Professor W. Wardlaw; November 13th, *Lecture*, "Diffusion in Biological Processes", by Dr. P. Eggleton; December 11th, *Lecture*, "Medico-legal Experiences", by Dr. G. Roche Lynch.

Eire. At Trinity College, Dublin: October 31st (joint meeting with the Werner Society), *Lecture*, "The Oxidation of Phenols", by Professor R. D. Haworth.

Exeter. At Washington Singer Laboratories: February 21st, *Lecture*, "Some Reactions of Free Radicals", by Dr. W. A. Waters; May 16th (joint meeting with the British Rheologists' Club), *Lectures*, "Clay", by Dr. G. Nagelschmidt, and "Rheology of Clay", by Mr. H. H. Macey; December 5th, *Lecture*, "Physico-chemical Problems of Insect Control", by Dr. A. B. P. Page.

Glasgow. February 21st, at the Royal Technical College, Annual General Meeting of the Local Section followed by the reading of papers; March 14th (joint meeting with the local sections of the Royal Institute of Chemistry and the Society of Chemical Industry), at the University, *Lecture*, "The Composition and Structure of Proteins", by Professor A. C. Chibnall; October 24th (joint meeting with the local sections of the Royal Institute of Chemistry and the Society of Chemical Industry), at the Royal Technical College, *Lecture*, "Some Aspects of the Chemistry of Fluorine", by Dr. B. C. Saunders; October 31st (joint meeting with the Alchemists' Club and the Andersonian Chemical Society), at the University, *Lecture*, "From the Highest to the Lowest", by Professor H. Nicol; November 21st (joint meeting with the local sections of the Royal Institute of Chemistryand the Society of Chemical Industry), at the Royal Technical College, *Lecture*, "Electron-transfer Reactions", by Professor M. G. Evans.

Hull. At University College: June 6th (joint meeting with the University College

Scientific Society), *Inaugural Lecture*, "Some Aspects of the Chemistry of Penicillin", by Sir Ian Heilbron; October 23rd (joint meeting with the local section of the Royal Institute of Chemistry and the University College Scientific Society), *Lecture*, "Addition Polymerisation", by Professor D. H. Hey; November 20th (joint meeting with the University College Scientific Society), *Lecture*, "The Structure of Proteins from the Viewpoint of the Chemist", by Professor A. C. Chibnall.

Leeds. February 25th (joint meeting with the University Chemical Society), at the University, *Lecture*, "The Chemistry of Penicillin", by Professor W. Baker, preceded by a display of scientific films.

Liverpool. At the University: January 23rd (joint meeting with the local sections of the Royal Institute of Chemistry, the Society of Chemical Industry, the British Association of Chemists, and the University Chemical Society), *Lecture*, "Metabolic Cycles", by Professor H. A. Krebs; February 20th (joint meeting with the Royal Institute of Chemistry, the Society of Chemical Industry, the British Association of Chemists, and the University Chemical Society), *Lecture*, "Recent Developments in the Chemistry of Starch and Glycogen", by Professor E. L. Hirst; February 27th (joint meeting with the local sections of the Royal Institute of Chemistry, the Society of Chemical Industry, and the British Association of Chemists), *Lecture*, "The Complete Analyst", by Mr. R. C. Chirnside; March 12th (joint meeting with the local sections of the Royal Institute of Chemistry, the Society of Chemical Industry, and the British Association of Chemists), Demonstration of scientific apparatus; November 20th (joint meeting with the local sections of the Royal Institute of Chemistry, the Society of Chemical Industry, the British Association of Chemists, and the University Chemical Society), *Lecture*, "The Chemistry of Ethylenic Polymers", by Professor H. W. Melville; November 27th (joint meeting with the local sections of the Royal Institute of Chemistry, the Society of Chemical Industry, and the British Association of Chemists), *Lecture*, "Penicillin", by Mr. G. A. Glister.

Manchester. January 9th (joint meeting with the local section of the Royal Institute of Chemistry), at the University, *Lecture*, "On Molecular Interaction at Oil–Water Interfaces", by Dr. J. H. Schulman; February 13th (joint meeting with the local section of the Royal Institute of Chemistry and the University Chemical Society), at the University, *Lecture*, "Some Aspects of the Chemistry of Fluorocarbons", by Professor M. Stacey; March 13th, at the University, *Meeting* for reading papers; April 17th (joint meeting with the local section of the Royal Institute of Chemistry), at the Engineers' Club, *Lecture*, "Recent Work in Colour Photography", by Mr. A. H. Baines; May 16th (joint meeting with the local sections of the Royal Institute of Chemistry and the Society of Chemical Industry), at the Engineers' Club, *Lecture*, "A New Notation for Organic Chemistry", by Dr. G. M. Dyson; October 9th, at the University, *Lecture*, "Inorganic Catalytic Halides", by Dr. F. Fairbrother; November 13th, at the University, *Meeting* for reading papers; December 5th (joint meeting with the local sections of the Royal Institute of Chemistry and the Society of Chemical Industry), at the University, *Lecture*, "Industrial Uses of Atomic Energy", by Sir Wallace Akers.

Newcastle and Durham. At King's College, Newcastle-on-Tyne: May 1st, *Meeting* for reading papers; May 9th, *Bedson Club Lecture*, "The Chemistry of Some Plant Gums and Mucilages", by Professor E. L. Hirst; October 17th, *Bedson Club Lecture*, "Some Aspects of Solid Reactions", by Professor W. E. Garner; November 14th, *Bedson Club Lecture*, "Pages from the Chemistry of Aluminium", by Professor H. Bassett; November 21st, *Meeting* for reading papers.

Northern Ireland. February 4th (joint meeting with the local section of the Royal Institute of Chemistry), at Queen's University, Belfast, *Lecture*, "Methods and Apparatus in Inorganic Microchemistry", by Mr. R. Belcher and Dr. C. L. Wilson.

North Wales. October 9th (joint meeting with the University College of North Wales Chemical Society), at University College of North Wales, Bangor, *Lecture*, "DDT and Gammexane in the Control of Insect-borne Diseases", by Sir Ian Heilbron.

Nottingham. At University College, January 23rd (joint meeting with the University College Chemical Society), *Lecture*, "Recent Advances in the Chemistry of the Enzymes",

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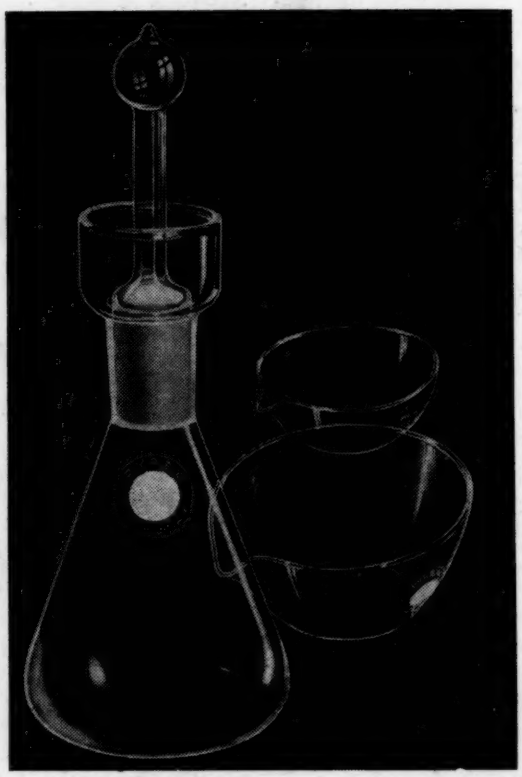

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